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# SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

| | |
|---|---|
| FIAN | Phys. Inst. Acad. Sci. USSR. |
| GDI | Water Power Inst. |
| GITI | State Sci.-Tech. Press |
| GITTL | State Tech. and Theor. Lit. Press |
| GONTI | State United Sci.-Tech. Press |
| Gosenergoizdat | State Power Press |
| Goskhimizdat | State Chem. Press |
| GOST | All-Union State Standard |
| GTTI | State Tech. and Theor. Lit. Press |
| IL | Foreign Lit. Press |
| ISN (Izd. Sov. Nauk) | Soviet Science Press |
| Izd. AN SSSR | Acad. Sci. USSR Press |
| Izd. MGU | Moscow State Univ. Press |
| LEIIZhT | Leningrad Power Inst. of Railroad Engineering |
| LET | Leningrad Elec. Engr. School |
| LETI | Leningrad Electrotechnical Inst. |
| LETIIZhT | Leningrad Electrical Engineering Research Inst. of Railroad Engr. |
| Mashgiz | State Sci.-Tech. Press for Machine Construction Lit. |
| MEP | Ministry of Electrical Industry |
| MES | Ministry of Electrical Power Plants |
| MESEP | Ministry of Electrical Power Plants and the Electrical Industry |
| MGU | Moscow State Univ. |
| MKhTI | Moscow Inst. Chem. Tech. |
| MOPI | Moscow Regional Pedagogical Inst. |
| MSP | Ministry of Industrial Construction |
| NII ZVUKSZAPIOI | Scientific Research Inst. of Sound Recording |
| NIKFI | Sci. Inst. of Modern Motion Picture Photography |
| ONTI | United Sci.-Tech. Press |
| OTI | Division of Technical Information |
| OTN | Div. Tech. Sci. |
| Stroiizdat | Construction Press |
| TOE | Association of Power Engineers |
| TsKTI | Central Research Inst. for Boilers and Turbines |
| TsNIEL | Central Scientific Research Elec. Engr. Lab. |
| TsNIEL-MES | Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants |
| TsVTI | Central Office of Economic Information |
| UF | Ural Branch |
| VIESKh | All-Union Inst. of Rural Elec. Power Stations |
| VNIIM | All-Union Scientific Research Inst. of Meteorology |
| VNIIZhDT | All-Union Scientific Research Inst. of Railroad Engineering |
| VTI | All-Union Thermotech. Inst. |
| VZEI | All-Union Power Correspondence Inst. |

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

А. Арбузов

# A NOTABLE JUBILEE

## (THE EIGHTIETH ANNIVERSARY AND FIFTY-FIFTH YEAR OF SCIENTIFIC ACTIVITY OF ACADEMICIAN A. E. ARBUZOV)

A. N. Pudovik

In September 1957 the chemical community of our country marked the eightieth anniversary and fifty-fifth year of scientific, teaching, and public activities of one of the oldest and most prominent scholars of our country, Academician Aleksander Erminigeldovich Arbuzov, who was twice awarded the Stalin Prize. As head of the Kazan chemical school for several decades, Arbuzov continued with great success the famous tradition established by the founders of this school, the eminent A. M. Butlerov and N. N. Zinin, and his brilliant investigations greatly increased its fame.

Owing to his inexhaustible interest in chemical science, his endeavor to solve the problems he set up, his widest scientific understanding, his great organizing talent, Arbuzov succeeded in giving to Kazan the Arbuzov School of Organic Chemists, which is now one of the most notable world chemical schools for the study of the chemistry of organic phosphorus compounds.

A. E. Arbuzov was born on August 31 (old style), 1877 in the village of Arbuzovo-Baran in the Kazan Government. After finishing at the First Kazan Gymnasium in 1896, Arbuzov entered the natural science division of the physicomathematical faculty. Even in his first course, when he heard the lectures of Professor F. M. Flavitsky, Arbuzov conceived a deep interest and love for chemistry. In the secondcourse, when he had finished the laboratory in quantitative analysis, Arbuzov began experimental work under the direction of A. Ya. Bogorodsky, investigating a titometric method for determining the higher degree of oxidation of manganese. In the third and fourth courses, under the influence of the interesting and profound lectures of A. M. Zaitsev, Arbuzov became absorbed in organic chemistry and under the guidance of his teacher, he began his first experimental work on the synthesis of allylmethylphenylcarbinol. It should be mentioned here that Arbuzov carried out the synthesis of this compound not only by the classical Butlerov-Zaitsev method using organic zinc compounds, but also by the new Grignard method with organomagnesium compounds. This first work of Arbuzov was published in 1901 [1]. In his student years Arbuzov began to study glass blowing and soon learned it well. His glass-blowing art, at which he became adept, helped him to construct a wide variety of original vessels and apparatus which he needed for his scientific investigations and which were widely known and accepted among organic chemists.

After finishing at Kazan University, Arbuzov, on the recommendation of Prof. F. M. Flavitsky, took the position of assistant to the chair of organic chemistry and agricultural analysis in the Novo-Aleksandriya Institute of Agriculture and Forestry. Here he worked with all the practical classes of the students, served as lecture assistant in the lectures on organic chemistry, and undertook the establishment of a laboratory. Arbuzov still found time for scientific work, however. At the suggestion of Prof. F. F. Selivanov, he began the study of the synthesis of tertiary butyl acetic acid. This turned out to be very difficult to carry out experimentally, and in spite of two years of persistent work he did not succeed in obtaining the desired substance. At the same time Arbuzov began to prepare for his Master's examination. While reading D. I. Mendeleev's "Fundamentals of Chemistry" Arbuzov's keen mind noticed the confused and contradictory data in the literature on the structure of phosphorus acid and its organic derivatives. This involved and complex question which disturbed the minds of many famous chemists of the time greatly interested Arbuzov and he resolved to choose it as the field for his own investigations.

There were two general views of the structure of phosphorus acid and its esters. Based on a study of the properties of the salts and the acid and neutral esters of phosphorus acid, Würtz, Michaelis, and Am considered phosphorus acid to be dibasic, with pentavalent phosphorus, while Graham, Railton, Wichelhaus, Zimmerman, and others considered it to be tribasic, with trivalent phosphorus. The same uncertainty existed as to the structure of phosphite esters. Interesting studies had been made on the structure of phosphorus acid by Russian chemists. N. A. Menshutkin had described their views in the sixties of the last century in the dissertation "Phosphorus Acid Hydrogen Which is Unavailable for Replacement by Metals Under Usual Conditions for Acids." The study of the structure and properties of phosphorus acid was carried on by G. G. Gustavson in the laboratory of D. I. Mendeleev and by F. M. Flavitsky at Kazan University.

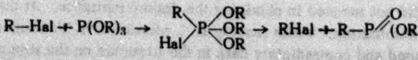
A number of circumstances made the solution of the interesting and important question of the structure of phosphorus acid and its esters difficult. The chief of these were the ignorance of a single easy method for converting the neutral phosphites into acid esters and the absence of a process by which esters of phosphorus acid could be prepared in a pure state. In this connection Arbuzov himself said ". . . Without going into details, I can say that not one of my predecessors in obtaining and studying esters of phosphorus acid with organic radicals knew how to prepare them. As I later showed, they described as these compounds what were mixtures of indefinite composition." It is also important to remember that before Arbuzov began his studies most chemists did not consider it possible to extend the structural theory of A. M. Butlerov to inorganic substances. This was because many elements, such as nitrogen, phosphorus, and sulfur in distinction to carbon have different valences in their compounds.

Being a firm and consistent supporter of A. M. Butlerov's structural theory, Arbuzov decided to reject ideas of the impossibility of using it for inorganic compounds and with great daring and energy he turned to the difficult question of the chemistry of phosphorus.

Repeating the experiments of his predecessors on the synthesis of phosphite esters, Arbuzov conclusively showed that they had not dealt with neutral esters, but with mixtures of these with dialkylphosphorus acid and esters of phosphoric acid. Arbuzov worked out a simple and reliable method of synthesis of neutral esters of phosphorus acid, involving the action of phosphorus trichloride on dry sodium alcoholates. With the pure esters at his disposal, Arbuzov proceeded to explain their structure. Even the first experiments on the action of bromine on the phosphite esters led Arbuzov to conclude that phosphorus was trivalent in them. Arbuzov finally solved this question by studying the reaction of different phosphorus compounds with metal salts. He succeeded in showing that cuprous halides give complex compounds, usually well crystallized, with most organic compounds of trivalent phosphorus. No compounds of pentavalent phosphorus react with cuprous halides. Thus he found a universal reagent with which he could simply and clearly solve the question of the valence of phosphorus in its different compounds. Since all the neutral phosphites gave complex compounds with cuprous halides, Arbuzov recognized them as compounds of trivalent phosphorus. Acid phosphites, and phosphorus acid itself, since they gave no complex compounds, were compounds of pentavalent phosphorus. Thus, with elegant simplicity, Arbuzov solved the question of the structure of phosphorus acid and its compounds — a question important for chemistry.

Later studies made by Arbuzov and his students as well as studies by other scholars fully confirmed the truth of Arbuzov's conclusions, made more than a half century before.

To explain the reason for the isomerization of the neutral esters of phosphorus acid from trivalent phosphorus into compounds of pentavalent phosphorus Arbuzov made a notable discovery — he found that such a transformation can occur under the influence of alkyl halides. The isomerization proceeds even in the presence of small amounts of alkyl halide so that Arbuzov could treat the process as catalytic. As a result of the isomerization the whole esters of phosphorus acid were transformed into esters of phosphinic acid. Arbuzov considered this process as proceeding in two stages. In the first phase the phosphite ester and the alkyl halide gave the unstable complex,



$$\mathrm{R{-}Hal + P(OR)_3 \rightarrow \overset{R}{\underset{Hal}{>}}P\overset{OR}{\underset{OR}{\leftarrow OR}} \rightarrow RHal + R{-}P{\overset{O}{/\!/}}(OR)_2}$$

which quickly broke down with formation of alkyl halide and the ester of alkyl phosphinic acid.

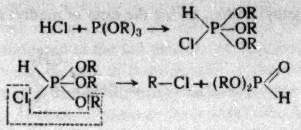
Thus by the action of methyl iodide on trimethyl phosphite, he obtained the dimethyl ester of methylphosphinic acid, and from triethyl phosphite and ethyl iodide the diethyl ester of ethylphosphinic acid. The reaction went smoothly and quantitatively at room temperature or with slight heating. Arbuzov further showed that the regrouping also occurred when the radical of the alkyl halide differed from the phosphite radicals. In the reaction of triethyl phosphite with methyl iodide or with propyl bromide he obtained the diethyl esters of methyl- or propylphosphinic acids, respectively. Thus he showed that isomerization of the phosphite esters under the influence of alkyl halides could serve as a simple method for the synthesis of different phosphinic esters. This famous reaction was later called the Arbuzov rearrangement.

Arbuzov showed the truth of his mechanism of the rearrangement by the example of the thermal decomposition of a substance which was stable under ordinary conditions, the product of combination of methyl iodide and triphenyl phosphite which had been obtained earlier by Michaelis and Jene. As a result of the decomposition he obtained iodobenzene and phenyl methylphosphinate.

With the help of this mechanism Arbuzov explained the course of the reaction of esters of phosphorus acid with hydrogen chloride. Before Arbuzov's work it was not clear how the action of water or alcohol on phosphorus trichloride formed derivatives of pentavalent phosphorus – phosphorus acid and its acid esters. Many chemists continued to consider the possibility of the existence of phosphorus acid in a trihydroxy form.

When he studied the action of hydrogen chloride on triethyl phosphite, Arbuzov showed that ethyl chloride and diethylphosphorus acid were formed, that is, the same products as were formed by the direct action of alcohol on phosphorus trichloride. Arbuzov represented the mechanism by the following scheme:

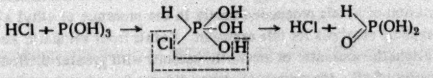
$$PCl_3 + 3ROH \rightarrow P(OR)_3 + 3HCl$$



Since the transformation of the neutral into the acid ester occurred with great ease by the action of hydrogen chloride, it became easily understandable why the action of phosphorus trichloride on alcohol did not give the neutral ester but instead, clearly enough, why the chief reaction product was the acid ester.

Arbuzov considered as analogous the formation of phosphorus acid from phosphorus trichloride and water.

$$PCl_3 + 3HOH \rightarrow P(OH)_3 + 3HCl$$

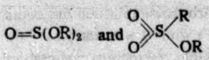


On the basis of these studies Arbuzov drew a very important conclusion as to the instability of compounds which contained hydroxyl on trivalent phosphorus, and as to their tendency to change into the isomeric compounds of pentavalent phosphorus which were more stable thermodynamically. In Arbuzov's opinion, hydroxyl compounds of trivalent phosphorus could be classed from their properties and behavior as of the same type as vinyl alcohol, if ". . . the double bond on the carbon atom is compared to the free affinities of the trivalent phosphorus."

These studies, which were carried out with such brilliance and elegance and which solved with clarity and completeness the important question of the chemistry of phosphorus, were combined and published by Arbuzov, as a monograph with the title "The Structure of Phosphorus Acid and Its Compounds" [2]. He presented it as a dissertation for the degree of Master of Chemistry and successfully defended it at Kazan University in 1905, the work attracting the attention of many famous chemists of the time. Because of the extreme importance of this investigation, the Russian Physicochemical Society awarded the dissertation the Zinin and Voskresensky Prize.

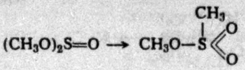
In 1906 after the retirement of F. F. Selivanov, Arbuzov was chosen by the Senate of the Novo-Aleksandriya Institute as adjunct professor in the chair of organic chemistry and agricultural analysis. Arbuzov continued to work chiefly in the field of phosphorus chemistry but he also showed great interest in other branches of organic chemistry. In the period from 1907-1914 Arbuzov and his students carried on interesting and extensive investigations on the structure and reactions of esters of sulfurous acid, the synthesis of acetals, and the catalytic decomposition of arylhydrazones of aldehydes and ketones. All these studies, in spite of their apparent diversity, were actually closely connected with the previous work of Arbuzov.

Observing the analogy between phosphorus and sulfurous acids and their esters, Arbuzov remarked [3] that "... just as with phosphorus acid there are two series of esters — esters corresponding to trihydroxyphosphorus acid and esters corresponding to alkyl phosphinic acid, so for sulfurous acid there are also two series of esters — esters corresponding to dihydroxysulfurous acid, and esters of alkyl sulfonic acid."



In developing his previous studies Arbuzov was most interested in the question of whether esters of sulfurous acid contained tetravalent sulfur and could react by combination and isomerization.

Arbuzov found that ethyl sulfite was easily saponified by solutions of dilute or concentrated alkali. When he studied the products immediately after saponification he found potassium sulfite, but when he studied them after a delay he found the anomalous product, potassium ethyl sulfonate. The mechanism of this interesting rearrangement was not explained. Of the different esters of sulfurous acid only the methyl ester showed the ability to isomerize when heated with methyl iodide, giving the ester of methyl sulfonic acid:



The difficulty in the isomerization of the esters was evidently related to their slight ability to undergo the addition reaction.

The work of Arbuzov with P. S. Pishchimuka [4] was devoted to methods for improving the preparation of aliphatic sulfonic acids; in the work with A. V. Kartashev [5] he considered the question of the existence of isomers of sulfurous acid double salts.

An interesting study was carried out by Arbuzov on the synthesis of ketals from orthoformic ester. In spite of the data of Claisen, Arbuzov established [6] that in ether solution orthoformic ester and ketones did not react with each other. Formation of ketals proceeded easily in the presence of ethyl alcohol or small amounts of mineral acid which were thus typical catalysts for this reaction. Ketals from aliphatic ketones were formed most easily by this method, from aliphatic-aromatic or aromatic ketones with greater difficulty, and from cyclic ketones with the greatest difficulty of all. Most cyclic ketones did not form ketals with orthoformic ester, but only the products of their decomposition, alcohol and esters of unsaturated alcohols. Later, Arbuzov investigated the synthesis of acetals of camphor [7] and cyclohexanone [8] and studied some of their transformations.

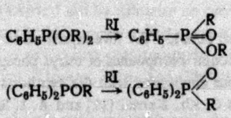
When studying the decomposition of aryl hydrazones of aldehydes and ketones [9], Arbuzov showed conclusively that the reaction of E. Fischer was catalytic and required for its occurrence the presence of only slight amounts of zinc chloride and not equimolecular amounts as E. Fischer had recommended. As catalysts for the Fischer reaction Arbuzov used cuprous halides which had already served him so well in studying the structures of phosphorus compounds. Arbuzov found that the decomposition of the hydrazones went differently depending on the size of the carbonyl residue: with small radicals indoles were formed, and with large radicals, nitriles were preferentially formed.

Arbuzov continued and developed his investigations in these fields in later years.

In 1911 after the death of A. M. Zaitsev, Arbuzov was chosen in an All-Russian competition of the Senate of Kazan University to take up the duties of extraordinary professor of organic chemistry. Following the tradition of his brilliant predecessors in this chair, A. M. Butlerov, N. N. Zinin, V. V. Markovnikov, and A. M. Zaitsev, Arbuzov quickly developed the scientific work in the laboratory, attracting to it all his co-workers, assistants, and students. The laboratory space was enlarged and reconstructed, electricity was introduced, drainage was constructed, etc. The intensity and sweep of the scientific activities of the laboratory are shown by the fact that in 1913 more than ten works appeared from it. Of these we may note "The Question of the Action of Bromine on Ether," a very exact and excellent example of experimental apparatus [10] and "Isobutyl Esters of Phosphorus Acid," in which an ingenious change of method led to obtaining pure esters [11].

The chief theme of Arbuzov's work in all these years continued to be the study of organophosphorus compounds. The opinions and ideas so brilliantly expressed in his Master's dissertation were expanded and deepened. In 1914 Arbuzov finished his doctoral dissertation and presented it to the Senate of Kazan University: "Catalytic Effects in the Field of Reactions of Some Phosphorus Compounds" [12]. In this great monograph Arbuzov described his experimental studies in condensed form, but at the same time with a full survey of studies on catalytic phenomena. Arbuzov, an adherent of the chemical theory of catalysis, showed conclusively that all isomerizations of trivalent phosphorus compounds into pentavalent substances proceeded through the formation of unstable intermediates which broke down during the reaction. Arbuzov came out against the view of Ostwald who considered only the energetics as important in catalytic processes.

In the development of the study begun in the Master's dissertation Arbuzov made a deep and many-sided investigation of the isomerization of esters of phosphorus acid with different radicals, and also of esters of phenylphosphinic and diphenylphosphinic acids and their sulfur analogs. Arbuzov showed that all these compounds which contained trivalent phosphorus isomerized in the presence of alkyl halides into compounds of pentavalent phosphorus. As the alkoxyl groups in the phosphite esters were replaced by phenyl radicals, the speed of isomerization increased considerably. Arbuzov took account of the fact that triphenyl phosphine has a strong tendency toward addition reactions and can be considered as the last member of the given series, and so he expressed the interesting idea of a direct relation between the rate of isomerization of phosphite esters and their ability to undergo addition reactions. An experimental test of this theory by the example of the addition of sulfur to phosphites fully confirmed Arbuzov's ideas. Addition of sulfur to the isobutyl ester of diphenylphosphinic acid occurred with the greatest speed; the diisobutyl ester of phenylphosphinic acid added it more slowly, and triisobutylphosphite added it most slowly of all. As a result of isomerizations of different esters of phenyl- and diphenylphosphinic acids, Arbuzov obtained different phosphine oxides.



$$C_6H_5P(OR)_2 \xrightarrow{RI} C_6H_5{-}P(R)(=O)(OR)$$

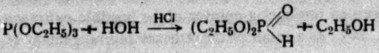
$$(C_6H_5)_2POR \xrightarrow{RI} (C_6H_5)_2P(=O)R$$

Analogous esters of diphenylthiophosphinic acid isomerized into the corresponding sulfides.

Arbuzov conducted a careful physicochemical study to explain the effect of temperature, nature of radicals in the ester groups, and halogens of the alkyl halides on the rate of isomerization.

As for ordinary chemical reactions, the rate of the catalytic isomerizations of the phosphite esters increased noticeably with temperature. As the radicals of the esters changed from light to those with greater molecular weight the rate of isomerization fell. The most active catalysts for the isomerization were the alkyl iodides; the least active were the chlorides.

In concluding his work, Arbuzov showed that saponification of the phosphite esters in the presence of water to dialkylphosphinic acids was a catalytic process. A very small amount of mineral acid served as the catalyst.



$$P(OC_2H_5)_3 + HOH \xrightarrow{HCl} (C_2H_5O)_2P(=O)H + C_2H_5OH$$

Thus by his experimental studies of the chemistry of organic phosphorus compounds, generalized in his Master's and Doctor's dissertations, Arbuzov solved a series of basic and important questions concerning the structure and reactivity of phosphorus and phosphinic acids and their esters and laid the foundation for further extended investigations in this field of chemistry so little known up to then.

The scientific activities of Arbuzov became especially wide and fruitful after the Great October Socialist Revolution which supplied all the conditions needed for successful development of science in our country. Arbuzov considered the need and demand to restore the national economy, and in the first years after the revolution conducted a series of investigations to aid native industry. He worked out a method of obtaining water-soluble nigrosine pigments which were needed for the tanning industry and a small factory was organized under his direction to produce these pigments.

Arbuzov made an interesting and practical investigation on the synthesis of furfurol from agricultural wastes which led to working out a simple method for obtaining this technically important product [13]. It is impossible not to note the work of Arbuzov, interesting both from a theoretical and practical viewpoint, on the chemical composition of pine resins and the methods he worked out for their practical use [14]. Besides the composition of galipot resin, he also studied the mechanism of its flow, and he determined the great pressures in a system of moving resin with a mercury manometer. This work of Arbuzov had great value in the organization of the turpentine industry in our country.

Along with his intensive scientific and teaching activities Arbuzov spent much time and strength in administrative and organizational work. He took an active part in 1930 in the creation of the Kazan Chemicotechnological Institute and organized the chair of organic chemistry in it. After the organization in 1929 of the A. M. Butlerov Chemical Scientific Research Institute at Kazan University, Arbuzov became its permanent director. Owing to his great organizing talent and energy, the Institute became a great chemical research center soon after its founding. After the opening of the Kazan branch of the Academy of Sciences in 1945 Arbuzov became Chairman of its Presidium and Director of the chemical institute. In this institute, Arbuzov organized the laboratory of organic chemistry which undertook the study of the chemistry of organic phosphorus compounds.

In his long years of work in Kazan University, in the Chemicotechnological Institute, and the Kazan branch of the Academy of Sciences, Arbuzov trained a great number of students who worked fruitfully with their teacher to develop Soviet science.

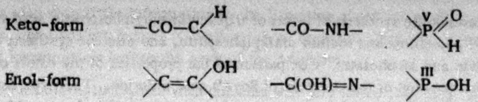
In this short paper, it remains possible to present only the important basic scientific directions explored by Arbuzov and his co-workers and to mention some of the more interesting investigations carried out in the last forty odd years.

In many studies Arbuzov continued to develop the investigations begun in his Master's and Doctor's dissertations. In work with A. V. Kartashev, molecular compounds of ethyl phosphite with silver halides were described [15]; with A. A. Ivanov he studied questions connected with the synthesis of isobutyl phosphite and gave a new method for obtaining it [16]; in work with G. Kh. Kamai [17] and A. I. Razumov [18] he continued to study the chemical properties of esters of phenylphosphorus and phenylphosphinic acids.

Especially interesting and important was the work carried out by Arbuzov on the further study of the rearrangement of phosphites. In this study Arbuzov and his students showed that not only alkyl halides could cause the Arbuzov rearrangement, but also esters of halogen substituted acids, haloketones, and other halogen compounds.

In the work of Arbuzov with A. A. Dunin [19], carried out even in 1914, he studied the reaction of triethyl phosphite with chlorinated esters, bromoacetates, esters of $\alpha$-bromopropionic acid or $\beta$-iodopropionic acid, and carried out the saponification to the free acid of the esters of the phosphonocarboxylic acids which he had synthesized. The esters of the phosphonocarboxylic acids were very interesting compounds, very similar in their properties to malonic and cyanoacetic esters. The action of metallic sodium on these esters resulted in substitution of the hydrogen in the methylene group by the metal; the action of alkyl halides on the metallic compounds formed alkyl derivatives of the phosphonocarboxylic esters [20]. In studying this reaction, Arbuzov and A. I. Razumov noticed that the halogen salts precipitated in quantities half as great as theory required. This finding led the authors to express an interesting opinion of the possible existence of the phosphonocarboxylic esters in tautomeric forms [21, 22]. As a result of the Arbuzov rearrangement of phosphite esters with bromoacetophenone, Arbuzov and Razumov obtained phosphoacetophenone, the first example of the phosphoketone series [23]. Phosphoacetophenone contained an active methylene group, since (like the phosphonoacetic esters) it easily formed metallic derivatives.

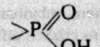
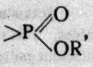
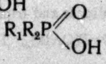
In the work "The Mechanism of the Double Decomposition of Metallic Compounds" [24], Arbuzov concluded that there was a great similarity in the reactions of metallic derivatives of dialkylphosphorus acid, keto-enols, and lactim-lactams with halogen derivatives of triaryl methanes and halogen derivatives of malonic ester, and he considered it possible to put into one series the study of the following groupings

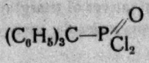


However, considering the great difficulties encountered in studying tautomeric effects by purely classical means, Arbuzov in the conclusions of his work mentioned the need for drawing on physicochemical methods in solving such questions. In his work with M. I. Batuev and V. S. Vinogradov [25] by a method of refraction he succeeded in showing that dialkylphosphorus acid in the liquid state exists as a mixture of two tautomeric forms with a great predominance of the form with pentavalent phosphorus.

The tendency of Arbuzov to use both chemical and physicochemical methods in solving some theoretical question was shown in many of his works.

Here we mention the work "Irreversible Endothermal Chemical Processes," in which Arbuzov studied the kinetics of hydrolysis of ketone acetals [26]; the work on compounds of ether with bromine [10] where he used a colorimetric method to study the possible existence at ordinary temperature of diethyl ether dibromide; the work carried out with A. A. Ivanov [27], to determine the atomic refraction of phosphorus in esters of phosphorus, phosphonic, and phosphoric acids; the study with P. I. Rakov [28] to determine the dipole moments of different types of organic phosphorus compounds, and a series of others [29]. In all these studies Arbuzov appears to us not only as an excellent organic chemist, but as a notable physical chemist, using physical methods with great skill for the study of organic compounds, showing great inventive capacity and originality in designing apparatus for conducting his planned experiments. Acquaintance with the work of Arbuzov shows his great keenness of observation, faultless accuracy and originality in setting up experiments, as well as his critical consideration of experimental data and conclusions.

An interesting investigation was carried out by Arbuzov on compounds which contained an asymmetrical phosphorus atom. In 1911 Meisenheimer and Lichtenstadt first succeeded in resolving phenylmethylethylphosphine oxide and methylphenylbenzylphosphine oxide into enantiomorphs [30]. All attempts to resolve asymmetrical hydroxyl compounds of phosphorus failed (Kipping, Pope, and Gibson). A. E. and B. A. Arbuzov considered the existence of optically active forms of phosphorus compounds with the groups  or  to be possible and began the study of phosphonocarboxylic acids of the general type , where one of the radicals $R_1$ or $R_2$ contained the carboxyl group [31]. Using their earlier method they synthesized phenylphosphonoacetic and phenyl-α-phosphonopropionic acids and tried to resolve them through the zinc salts. The experiments did not give positive results. Arbuzov and G. Kh. Kamai [32] failed to resolve compounds of the general type $R_1R_2PS(OH)$ and $R_1R_2PS(SH)$.

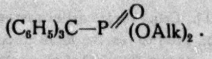
Among the studies of Arbuzov which were most important both in results and especially in consequences was the investigation designed to explain the structure of the acid chloride of Boyd, carried out with B. A. Arbuzov [33]. In 1923 Boyd [34] treated an excess of phosphorus trichloride with triphenyl carbinol and obtained a compound which he thought was a derivative of trivalent phosphorus $(C_6H_5)_3C-O-PCl_2$. This acid chloride, however, in distinction to the well-known acid chloride studied earlier by Menshutkin $RO-PCl_2$ (where R is alkyl or aryl), was especially stable to the action of air, water, and even caustic alkalis. When the acid chloride was saponified by alcoholic potassium hydroxide it did not give the triphenylmethyl ester of phosphorus acid, as would be expected from the structure assumed by Boyd, but triphenylmethyl phosphinic acid. According to Boyd, the hydrolysis was accompanied by a molecular rearrangement consisting of the shift of the triphenylmethyl group from oxygen to phosphorus and the change of phosphorus from trivalent to pentavalent. A critical consideration of Boyd's theoretical structure led Arbuzov to a justified doubt of Boyd's idea of the acid chloride structure. Arbuzov expressed the opinion that Boyd's compound had a different structure and contained pentavalent phosphorus bound directly to the carbon of the triphenylmethyl radical  $(C_6H_5)_3C-P\overset{O}{\underset{Cl_2}{\diagup}}$ To decide this question, A. E. and B. A. Arbuzov undertook the synthesis of esters of triphenylmethylphosphinic acid starting from triphenylbromomethane, trialkyl phosphites and sodium dialkylphosphite, and also the synthesis of phosphite esters starting from Boyd's acid chloride and alcoholates. Comparison of the properties of the esters obtained by the different methods would solve the question of the structure of Boyd's acid chloride. The experiments showed that the properties of Boyd's compound were those of a substance with pentavalent phosphorus, although a final solution of the problem was not reached. Attempts to replace both atoms of chlorine in Boyd's acid chloride by ethoxy groups failed; in all cases only one atom of chlorine was replaced by an ethoxy group. The action of phosphite esters on triphenylbromomethane gave methyl or other (up to isobutyl) esters of triphenylmethylphosphinic acid. Saponification of the chloroesters obtained from Boyd's acid chloride and esters of triphenylmethylphosphinic acid gave the same triphenylmethylphosphinic acid. Later the structure of the acid chloride as a compound of pentavalent phosphorus was finally established by Hatt, one of Boyd's students.

While studying the reactions of Boyd's acid chloride, A. E. and B. A. Arbuzov made a very important discovery. They showed that the reactions of triphenylchloromethane and triphenylbromomethane with sodium diethylphosphite went entirely differently. In the first case they obtained the diethyl ester of triphenylmethylphosphinic acid, identical with that obtained earlier from triphenylchloromethane and triethylphosphite, while in the reaction with triphenylbromomethane they obtained the completely unexpected triphenylmethyl peroxide. When they ran the reaction in ether solution in a stream of nitrogen they obtained a good yield of "triphenylmethyl" as its ether complex. Thus A. E. and B. A. Arbuzov discovered a new, very interesting, and elegant method for obtaining free radicals [35].

$$(C_6H_5)_3CBr + NaOP(OR)_2 \rightarrow (C_6H_5)_3C\cdot + (RO)_2PO\cdot + NaBr$$

When they replaced triphenylbromomethane by diphenyl-α-naphthylbromomethane they obtained diphenyl-α-naphthylmethyl.

The reaction of sodium diethylphosphite with bromomalonic ester evidently also proceeded through a free radical step; as the chief reaction product was obtained an ester of ethane tetracarboxylic acid [36]. Obtaining free radicals by the Arbuzov method is so simple and cheap that it makes this reaction widely available for lecture demonstrations.

Potassium, lithium, rubidium and cesium dialkylphosphites also give free radicals with triarylmethyl bromides. The silver salts behave differently. When the reaction is run with silver dialkylphosphites which contain different radicals and triphenylmethyl chloride is used, it always gives a mixture of esters of the general type $(C_6H_5)_3C-O-P(OAlk)_2$. The analogous reaction with triphenylbromomethane leads to formation of triarylmethylphosphinic acids  $(C_6H_5)_3C-P\overset{O}{\underset{(OAlk)_2}{\diagup}}$.

The question of the fate of the part which contains phosphorus in free radical formation is of great interest. Attempts to separate the phosphorus-containing part from the products of reaction of triphenylmethyl bromide and sodium diethylphosphite did not succeed due to experimental difficulties. Considering that the phosphonic radicals formed in the reaction were not capable of long existence and when they dimerized were most probably converted to ethyl subphosphate, A. E. and B. A. Arbuzov began to study the action of bromine on sodium diethylphosphite [37]. In this reaction they expected the formation of esters of hypophosphoric acid without any byproducts as impurities.

$$2(C_2H_5O)_2PONa + Br_2 \rightarrow [(C_2H_5O)_2PO]_2 + 2NaBr$$

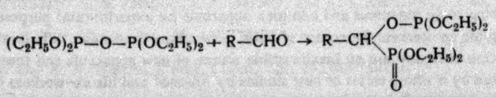
However, careful and repeated trials showed that the reaction was very complex and besides the formation of subphosphate esters, which were the chief products, led to ethyl esters of pyrophosphoric, pyrophosphorus, phosphoric and phosphorus acids. A. E. and B. A. Arbuzov distilled them repeatedly in a vacuum from a special apparatus invented and constructed by Arbuzov and for the first time separated pure esters of hypophosphoric, pyrophosphoric, and pyrophosphorus acids, studied their different reactions, and established the mechanism of their formation. The significance of this investigation becomes clear if we mention that although hypophosphoric acid had been known since the time of Pelletier (1792) and its esters were first described by Zenger (1886), this compound had never been obtained pure before the work of the Arbuzovs, and the question of its structure remained open. There was also very little information in the literature about esters of pyrophosphoric acid: they were described as viscous, nondistilling liquids (Cavalier) whose constants were not determined. Esters of pyrophosphorus acid were not known at all before the work of the Arbuzovs.

The reaction of sodium diethylphosphite with chlorine was very interesting [38]. Aside from the expected hypophosphoric, the chief reaction product was ethyl pyrophosphate and in small amount they obtained the acid chloride of diethylphosphorus acid. Compounds of the type $(RO)_2PCl$, as distinct from the acid chlorides $ROPCl_2$ obtained earlier by Menshutkin and already well studied, had not been known before the work of the Arbuzovs. The action of the acid chloride of diethylphosphorus acid on sodium diethylphosphite gave ethyl pyrophosphite. Further study of this interesting compound was carried on by Arbuzov and his co-workers A. I. Razumov [39], V. S. Abramov [40], and P. I. Alimov [41] in later years. An especially wide range of studies of esters of hypophosphoric, pyrophosphoric, and pyrophosphorus acids was carried out under the direction of Arbuzov in the Kazan branch of the Academy of Sciences of the USSR. These studies, begun in 1946, have been successfully continued until the present. Many of the compounds which have been synthesized have shown very interesting and valuable properties as insecticides and physiologically active substances.

Arbuzov and his co-workers have carefully worked out improved methods of synthesis of ethyl pyrophosphates and have studied its chemical properties. This compound, first obtained by A. B. and B. A. Arbuzov in 1931, has a strong toxic action for many forms of harmful insects. The acid amide and different thioanalogs have been synthesized, many of which have great interest as insecticides. It was shown that esters of pyrophosphoric acid can be easily obtained by oxidation in air of esters of pyrophosphorus and hypophosphoric acid [42]. The preparation of esters of pyrophosphorus acid was considerably simplified and improved [43]. The action of hydrogen chloride [44] split them into dialkylphosphorus acid and its chloride; the action of fatty acids on ethyl pyrophosphite gave along with diethylphosphorus acid a mixed anhydride of diethylphosphorus acid and the carboxylic acid [45].

$$(C_2H_5O)_2P{-}O{-}P(OC_2H_5)_2 + HOOC{-}R \rightarrow (C_2H_5O)_2POH + (C_2H_5O)_2POCOR$$

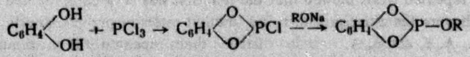
By the action of different aldehydes on tetraethyl pyrophosphite [46] compounds were synthesized which contained tri- and pentavalent phosphorus.



$$(C_2H_5O)_2P{-}O{-}P(OC_2H_5)_2 + R{-}CHO \rightarrow R{-}CH\left\langle\begin{array}{l} O{-}P(OC_2H_5)_2 \\ \underset{\underset{O}{\|}}{P}(OC_2H_5)_2 \end{array}\right.$$

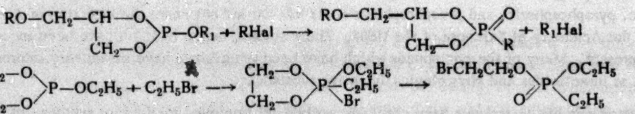
In 1951 Arbuzov turned again to the question of the composition of the phosphorus-containing part formed in the preparation of free radicals by the Arbuzov method. With F. G. Valitova [47] he found in the reaction products from triphenylmethyl bromide and sodium diethylphosphite the ethyl ester of hypophosphoric acid.

One of the most interesting investigations by Arbuzov, which has been especially developed in recent decades, is the study of cyclic phosphites. Studies of pyrocatechol phosphites were begun by Arbuzov with F. G. Valitova in 1934. They found a simple and accessible method of synthesis of pyrocatechol phosphoromonochloride [48] by the action of phosphorus trichloride on pyrocatechol; this allowed them to synthesize several hundred grams of the product with a yield of 90% in a day's work. The action of alcoholates on the chloride gave different esters of pyrocatecholphosphorus acid



The alkylpyrocatechol esters easily form complexes with cuprous halides; the methyl and ethyl esters are isomerized by alkyl iodides to pyrocatechol esters of methyl- and ethylphosphinic acids. The latter add a molecule of water with evolution of a considerable amount of heat. By the action of sodium diethylphosphite on pyrocatecholphosphoromonochloride Arbuzov and F. G. Valitova obtained the pyrocatechol diethyl ester of phosphorus acid and studied its properties.

The study was widened by Arbuzov and V. M. Zoroastrova, N. I. Rizpolozhensky, and M. M. Azanovskaya, obtaining alicyclic esters of phosphorus acid [49, 50]. The action of phosphorus trichloride on ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butylene glycol, and diethylene glycol gave cyclic chlorides containing 5 to 8 atoms in the ring. The action on the chlorides of alcohol in the presence of bases gave cyclic esters of phosphorus acid. Besides the usual reactions of phosphite esters (formation of complexes with cuprous halides, addition of sulfur) they showed unusual properties in reactions with halogen compounds. In one case this reaction goes with preservation of the ring, and in the other with splitting of it.



On the basis of studies of analogous reactions with different cyclic esters, Arbuzov was able to explain some regularities in their course, depending on the structures of the cyclic esters. Analogously to the cyclic oxygen esters, Arbuzov and V. M. Zoroastrova obtained dithioethanephosphorus acid chloride, starting from thiodiglycols, and studied its properties [51].

This short account of the scientific activities of Arbuzov shows how he grew and developed. Besides his fundamental studies of organophosphorus compounds, which we have described, and his work on sulfite esters, catalytic decomposition of ketone hydrazones, study of resins, and physicochemical investigations, we should add also the brilliant work on tautomeric compounds of isatin [52], carbostyril [53], acid amides [54], the study of the reducing action of magnesium organic compounds [55], and others.

In spite of his age and the great load of administrative work Arbuzov maintains a lively interest in chemical events; he can constantly be seen in the laboratory, animatedly discussing with his co-workers and students the progress of chemistry and the results of particular experimental investigations. Arbuzov can often be seen at the workbench making some ingenious and complex apparatus for experimental purposes, or on the laboratory stool, discovering with his co-workers the course of some particular experiment. His lively, keen mind and amazing powers of observation even now are an inexhaustible source of new apparatus and interesting investigations. Recent years are marked by a whole series of new studies by Arbuzov and his co-workers in the field of the chemistry of organic phosphorus compounds.

Arbuzov and M. M. Azanovsky [56] studied the reaction between acetyl chloride and sodium diethylphosphite and discovered an addition reaction of dialkylphosphorus acids to the carbonyl group, later expanded in the work of V. S. Abramov.

In work with F. G. Valitova [57] and N. A. Razumov [58] he found new data on cyclic phosphites; with V. M. Zoroastrova he obtained and studied complex compounds of neutral esters of phosphorus acid with salts of copper, silver, gold [59], platinum [60], and mercury [61]; with L. V. Nesterov he isolated a whole series of new, stable complexes of triphenyl phosphite with different alkyl iodides and studied their thermal decomposition [62]. Arbuzov and M. G. Imaev have recently obtained interesting data [63] on the saponification of phosphites in the presence of water. They showed the accelerating action of dialkylphosphorus acids and the slowing action of inorganic and organic bases on the hydrolysis. They accomplished the synthesis of mixed phosphites by partial transesterification and studied their properties. They obtained new and interesting data on the double decomposition of isatin with metallic compounds [53]; with Yu. P. Kitaev, Arbuzov conducted an original study of the mechanism of catalytic decomposition of hydrazones.

Arbuzov is one of the most prominent historians of chemistry of our country. His excellent papers on many famous Russian chemists and his monograph "A Short Sketch of the Development of Organic Chemistry in Russia," [64] which unites a deep historical analysis of events with a simple and expressive form, will always be read with interest and gratitude by Soviet chemists.

A characteristic feature of all the activities of Arbuzov is his constant effort to extend the attainment of chemistry among all the workers of our country. Arbuzov has been the organizer of many scientific meetings both in Kazan and outside of it and has taken an active part in the work of the Mendeleev All-Union Chemical Society. Since 1930 Arbuzov has been permanent president of the Kazan Section of the Society.

For his classical and fundamental work in organic chemistry and particularly on organic phosphorus compounds, Arbuzov was chosen in 1932 as a Corresponding Member, and in 1942 as an Active Member of the Academy of Sciences of the USSR; he twice received the Stalin Prize. The government has highly honored Arbuzov's services in developing science and in professional training, awarding him the double order of Lenin and the Order of the Red Banner of Labor. In 1935 Arbuzov was given the honorary title of one distinguished in science of the RSFSR. A. E. Arbuzov is highly respected and popular among the workers of the Tartar Republic. He was three times chosen deputy in the Council of Republics of the Supreme Soviet of the USSR.

## LITERATURE CITED

[1] A. E. Arbuzov, J. Russ. Chem. Soc. 33, 38 (1901).

[2] A. E. Arbuzov, The Structure of Phosphorus Acid and Its Derivatives (Novo-Aleksandriya, 1905).*

[3] A. E. Arbuzov, J. Russ. Chem. Soc. 41, 429 (1909).

[4] A. E. Arbuzov and P. S. Pishchimuka, J. Russ. Chem. Soc. 41, 451 (1909).

[5] A. E. Arbuzov, J. Russ. Chem. Soc. 41, 447 (1909); A. E. Arbuzov and A. V. Kartashev, J. Russ. Chem. Soc. 46, 284 (1914).

[6] A. E. Arbuzov, J. Russ. Chem. Soc. 40, 637 (1908).

[7] A. E. Arbuzov, J. Russ. Chem. Soc. 61, 1595 (1929).

[8] A. E. Arbuzov and B. M. Mikhailov, J. Gen. Chem. 6, 390 (1936).

[9] A. E. Arbuzov and V. M. Tikhvinsky and others, J. Russ. Chem. Soc. 45, 70, 74, 694, 697, 699 (1913); A. E. Arbuzov and V. A. Rotermal, J. Gen. Chem. 2, 397 (1932); A. E. Arbuzov and I. A. Zaitsev, Trans. Kazan Chem. Tech. Inst. 1, 33 (1934); A. E. Arbuzov, I. A. Zaitsev, and A. I. Razumov, J. Gen. Chem. 6, 289 (1936).

[10] A. E. Arbuzov, J. Russ. Chem. Soc. 45, 442 (1913).

[11] A. E. Arbuzov and A. A. Ivanov, J. Russ. Chem. Soc. 45, 681 (1913).

[12] A. E. Arbuzov, Catalytic Effects in the Field of Reactions of Some Phosphorus Compounds (Kazan, 1914).*

[13] A. E. Arbuzov and B. P. Lugovkin, J. Appl. Chem. 7, 550 (1934).

[14] A. E. Arbuzov, Tech. Econ. Herald 5, 626 (1925).

[15] A. E. Arbuzov and A. V. Kartashev, J. Russ. Chem. Soc. 45, 79 (1913).

[16] A. E. Arbuzov and A. A. Ivanov, J. Russ. Chem. Soc. 45, 681 (1913).

[17] A. E. Arbuzov, G. Kh. Kamai, and O. N. Belorossova, J. Gen. Chem. 15, 766 (1945).

[18] A. E. Arbuzov and A. I. Razumov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1945, 167.

[19] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc. 46, 295 (1914).

---

* In Russian.

[20] A. E. Arbuzov and A. I. Razumov, J. Russ. Chem. Soc. 61, 623 (1929).

[21] A. E. Arbuzov and A. I. Razumov, J. Gen. Chem. 4, 834 (1934).

[22] A. E. Arbuzov and A. I. Razumov, Trans. Kazan Chem. Tech. Inst. 10, 35 (1946).

[23] A. E. Arbuzov and A. I. Razumov, J. Gen. Chem. 4, 834 (1934).

[24] A. E. Arbuzov, Trans. Acad. Sci. USSR Session on Organic Chemistry, 1939.

[25] A. E. Arbuzov, M. I. Batuev, and V. S. Vinogradova, Proc. Acad. Sci. USSR 54, 603 (1946).

[26] A. E. Arbuzov, J. Russ. Chem. Soc. 59, 357 (1927).

[27] A. E. Arbuzov and A. A. Ivanov, J. Russ. Chem. Soc. 47, 2015 (1915).

[28] A. E. Arbuzov and P. I. Rakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, 237.

[29] A. E. Arbuzov, J. Russ. Chem. Soc. 59, 357 (1927).

[30] J. Meisenheimer and Lichtenstadt, Ber. 44, 356 (1911).

[31] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Chem. Soc. 61, 1599 (1929).

[32] A. E. Arbuzov and G. Kh. Kamai, J. Russ. Chem. Soc. 61, 2034(1929).

[33] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Chem. Soc. 61, 217 (1929).

[34] Boyd and Chignell, J. Chem. Soc. 123, 813 (1923).

[35] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Chem. Soc. 61, 1923 (1929).

[36] A. E. Arbuzov and V. S. Abramov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 223.

[37] A. E. Arbuzov and B. A. Arbuzov, J. Gen. Chem. 2, 345, 368 (1932).

[38] A. E. Arbuzov and B. A. Arbuzov, J. Gen. Chem. 2, 371 (1932).

[39] A. E. Arbuzov and A. I. Razumova, J. Gen. Chem. 7, 1762 (1937).

[40] A. E. Arbuzov and V. S. Abramov, Bull. Kazan Chem. Tech. Inst. 1, 28 (1935).

[41] A. E. Arbuzov and P. I. Alimov, Bull. Kazan Fil., Acad. Sci. USSR 1, 21 (1950).

[42] A. E. Arbuzov and P. I. Alimov, Bull. Kazan Fil., Acad. Sci. USSR 1, 31 (1950).

[43] A. E. Arbuzov, Bull. Kazan Fil., Acad. Sci. USSR 1, 14 (1950).

[44] A. E. Arbuzov and P. I. Alimov, Bull. Kazan Fil., Acad. Sci. USSR 1, 31 (1950).

[45] A. E. Arbuzov and P. I. Alimov, Bull. Kazan Fil., Acad. Sci. USSR 1, 21 (1950).

[46] A. E. Arbuzov and P. I. Alimov, Bull. Kazan Fil., Acad. Sci. USSR 1, 17, 31 (1950).

[47] A. E. Arbuzov and F. G. Valitova, Proc. Acad. Sci. USSR 83, 4 (1952).

[48] A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1940, 529.

[49] A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1948, 208; 1950, 357.

[50] A. E. Arbuzov and M. M. Azenovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1949, 473.

[51] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 453.*

[52] A. E. Arbuzov and M. Sh. Bastanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 459.*

[53] A. E. Arbuzov and M. Sh. Bastanova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 831.*

[54] O. M. Shapshinskaya, Dissertation,(Kazan, 1942).

---

* Original Russian pagination. See C.B. Translation.

[55] A. E. Arbuzov and I. A. Arbuzova, J. Gen. Chem. 2, 388 (1932).

[56] A. E. Arbuzov and M. M. Azanovskaya, Proc. Acad. Sci. USSR 58, 1961 (1947).

[57] A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 681.*

[58] A. E. Arbuzov and N. A. Razumova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 187.*

[59] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 809.*

[60] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 818.*

[61] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 826.*

[62] A. E. Arbuzov and L. V. Nesterov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 427.*

[63] A. E. Arbuzov and M. G. Imaev, Proc. Acad. Sci. USSR 112, 856 (1957).*

[64] A. E. Arbuzov, A Short Sketch of the Development of Organic Chemistry in Russia, Izd. AN SSSR, 1948.**

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* Original Russian pagination. See C. B. Translation.

** In Russian.

# SYNTHESES OF HETEROCYCLIC COMPOUNDS BASED ON THE FISCHER REACTION

## I. THE MECHANISM OF THE FISCHER REACTION

A. E. Arbuzov and Yu. P. Kitaev

In 1883 E. Fischer and F. Jourdan [1] established that heating pyruvic acid methylphenylhydrazone with an alcohol solution of hydrogen chloride gave a low yield of a nitrogen compound, which was found to be 1-methylindole-2-carboxylic acid [2]. Later E. Fischer investigated this reaction more thoroughly, using zinc chloride as the condensing agent [3] and extended this reaction to cover arylhydrazones of aldehydes, ketones and ketoacids [4].

In 1910 one of us investigated the complex compounds of cuprous halides with various nitrogen bases and, among others, obtained unstable compounds with phenylhydrazine [5]. The exceptionally easy thermal decomposition of these complexes raised the question of whether salts, that form unstable complexes with phenylhydrazine, could act as catalysts in the Fischer reaction. This idea was checked experimentally and confirmed with V. M. Tikhvinsky [6].

It was the first time that the Fischer reaction was proved to have a catalytic character and, in connection with this, substantial changes were made in the Fischer method. It was found that instead of 5-fold excess by weight of zinc chloride, 0.4-0.8 g of $ZnCl_2$, $Cu_2Cl_2$, $PtCl_4$ or $Cu_2Br_2$ could be used for the reaction per mole of hydrazone. Then and in the following years, together with V. I. Tikhvinsky, A. I. Razumov, I. A. Zaitsev, et al., a whole series of substituted indoles was prepared in good yields by this method [6-12].

The discovery and proof of the catalytic character of the Fischer reaction started a search for new catalysts and work in this direction turned out to be very fruitful. Up to the present time thirty catalysts have been proposed and among them are various concentrated and dilute acids, alcoholic acid solutions, polyphosphoric acid, many metal halides, metal powders, boron trifluoride, Grignard reagents and ion-exchange resins. Generally, acidic reagents and, apparently, substances capable of forming complexes are catalysts for the Fischer reaction.

The reaction discovered by Fischer has become the cornerstone of a practical laboratory method for a series of syntheses in the field of nitrogen-containing heterocyclic compounds. It is hard to overestimate the value of this method in synthestic organic chemistry – it gave investigators hundreds of new compounds, interesting either in themselves or as intermediates for the preparation of dyes, drugs, aromatic principles and other valuable compounds. The Fischer method is now used to prepare substituted indoles, indolenines, oxindoles [13], tetrahydro- [14] and octahydrocarbazoles [15], pyrroles [16], tri- and tetracyclic azazulenes [17] and 2-aminobenzthiazole [18].

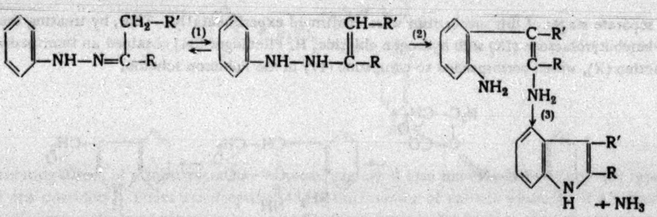
The Fischer reaction has been applied to about sixty different arylhydrazines and it is likely that many more examples of the above classes will be successfully prepared by Fischer's method. Of the carbonyl compounds, the most varied aldehydes, ketones, aldehyde and ketoacids and their esters and also naphthols, coumarones and ketolactones were used in the reaction. Some limits are known in the selection of arylhydrazones: thus, dinitroindoles cannot be prepared from 2,4-dinitrophenylhydrazones, and a case is described where an indole was not obtained from hydroxyphenylhydrazone [19]. Also an indole could not be prepared from acetaldehyde phenylhydrazone [20].

Even though more than 70 years have passed since the discovery of the Fischer reaction, the mechanism of this interesting reaction has not yet been completely elucidated, although many investigators have studied this problem [21-32]. The mechanism scheme proposed by G. and R. Robinson [23] is the most widely accepted at the present time, although the basic hypothesis of this scheme – o-benzidine rearrangement – was put forward by K. Brunner in 1898 [21]. The Robinsons divide the reaction into three main stages:

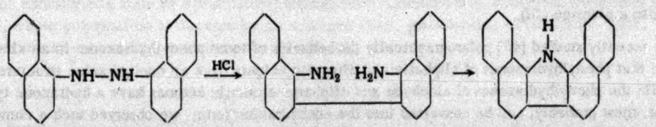
1) conversion of the hydrazone into an enehydrazine, which they consider occurs on the addition of an acidic reagent and is a ketimide-enamine isomerization;

2) enehydrazine rearrangement of the ortho-benzidine type;

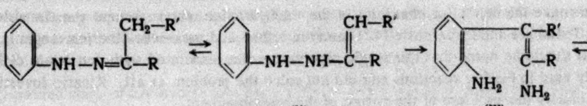
3) ring formation with elimination of an ammonium salt, similar to the formation of piperidine from pentamethylenediamine hydrochloride



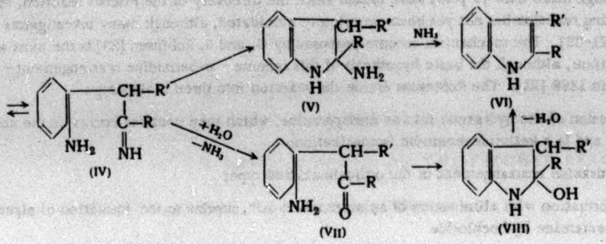
According to the Robinsons, an acid medium and a high temperature are necessary for all the stages as each successive compound has a more basic character than the preceding one. Ring closure ends this process of growing basic properties. The authors substantiated their scheme in the following way: having drawn an analogy between the first stage and enolization of the carbonyl compounds, they found that the more readily the carbonyl compound was enolized, the more readily its phenylhydrazone was converted into indole. The second and third stages also have analogs – rearrangement of hydrazonaphthalene, which was observed by R. Nietzki and O. Goll [33].



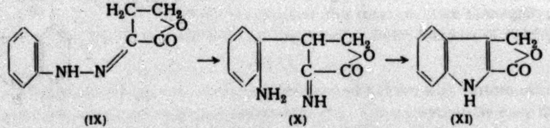
The ortho-benzidine rearrangement and that of arylhydrazones in the Fischer reaction were explained by the authors using fractional valences, which arise at the nitrogen in the formation of arylhydrazone salts. Later on the Robinsons themselves, and then K. Allen and K. Wilson [28] supplemented the first scheme of the mechanism and it acquired the following final form



(I) (II) (III)



The separate stages of this mechanism were confirmed experimentally. Thus, by treating the phenylhydrazone of α-ketobutyrolactone (IX) with hydrogen chloride, H. Plieninger [34] obtained an intermediate of the Fischer reaction (X), which corresponded to compound (IV) in the Robinson scheme.



When heated for a short time with acetic acid this product gave the lactone of 3-hydroxymethylindolecarboxylic acid (XI) [35]. The intermediate product (IV) was also isolated by decomposing the phenylhydrazone of camphenilone [36]. The hydrolysis of the intermediate was confirmed by observation [37-39].

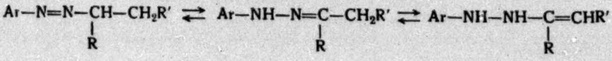
Thus, almost all the stages of the mechanism proposed by G. and R. Robinson and supplemented by K. Allen and K. Wilson, were considered plausible, except for the initial ones, i. e., the basic ones, namely the tautomeric conversion of the hydrazone into an enehydrazine (II) and the rearrangement of this hypothetical enehydrazine into a diamine (III).

We recently studied [40] polarographically the behavior of some phenylhydrazones in an alcohol solution and found that phenylhydrazones of aliphatic and alicyclic ketones have an enehydrazine structure in the free state, while the phenylhydrazones of aldehyde and aliphatic-aromatic ketones have a hydrazone type of structure. The latter, most probably, can be converted into the enehydrazine form: we observed such a conversion, for example, with acetaldehyde phenylhydrazone. In this way, our work in this direction proved the accuracy of the first stage of the Robinson scheme.

The absence of para-rearrangement products in the whole range of Fischer reactions investigated is still not quite explained. Furthermore, substituents in the para-position in the arylhydrazine nucleus not only do not increase the indole yield, but often even make its formation difficult [41].

These facts make the benzidine character of the enehydrazine rearrangement questionable [25]. It is true that recently W. Teilacker and O. Leichtle [42] observed ortho- and para-semidine rearrangement of some phenylhydrazones, but it should be noted that this single observation was associated with conditions different from the conditions usually used in Fischer reactions and did not solve the problem at all. Kinetic investigations [43, 44] likewise did not clarify the problem of the nature of the rearrangement.

Lately ideas on the general theory of conjugation have been increasingly accepted in organic chemistry. Various 1,4-conjugated systems have been quite widely and thoroughly studied [45, 46]. Having established that arylhydrazones may, in general, exist in the following three tautomeric forms

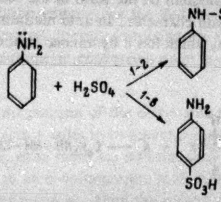


$$\underset{\textstyle R}{Ar{-}N{=}N{-}\underset{|}{C}H{-}CH_2R'} \rightleftarrows \underset{\textstyle R}{Ar{-}NH{-}N{=}\underset{|}{C}{-}CH_2R'} \rightleftarrows \underset{\textstyle R}{Ar{-}NH{-}NH{-}\underset{|}{C}{=}CHR'}$$

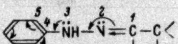
we decided to elucidate, from the point of view of the general theory of conjugation the reactions of the bonds in the hydrazone and enehydrazine forms.

Hydrazone molecules contain a system that includes two nitrogen atoms, one of which is connected to a carbon atom by a multiple bond $>C{=}\underset{|}{C}{-}\underset{|}{\ddot{N}}{-}\ddot{N}{=}C<$.

It is known that the pair of unshared electrons of a nitrogen, oxygen or sulfur atom, in a position $\alpha$ to an ethylene bond, becomes conjugated with the latter [47]. The chemical manifestation of the conjugation of the free pair of electrons of a nitrogen atom with multiple bonds is double reactivity, for example, of aniline [46]



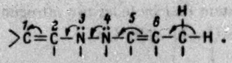
The orienting effect of a substituent in a benzene nucleus is also sometimes caused by this type of conjugation. If one considers F. Ender's conception [48] of the reaction of valence electrons of a carbon atom with the electrons of a more electronegative atom, named induced conjugation by him, then the reaction of a multiple bond with free electrons, for example, of a nitrogen atom, may be shown in the following way. The electrons of the $C-\ddot{N}$ bond are displaced towards N, while the electron cloud of the carbon atom is deformed, due to which the electron cloud of the following carbon atom becomes more stable, and the whole system is a succession of disturbed and stabilized electron octets, i. e., in the system $-\underset{|}{\overset{6}{C}}{=}\underset{|}{\overset{5}{C}}{-}\underset{|}{\overset{4}{C}}{=}\underset{|}{\overset{3}{C}}{-}\underset{|}{\overset{2}{C}}{=}\underset{|}{\overset{1}{C}}\rightarrow\ddot{N}-$ , atoms 2, 4 and 6 are more electronegative than 1, 3 and 5. Due to the polarity of the C−N bond, the free electron pair of nitrogen becomes more labile and, reacting with the $\pi$-electrons of the multiple bond, strengthens the induced conjugation and establishes a state of $\pi$p-structural conjugation. Consequently, hydrazone molecules contain a $\pi$p$\pi$-system, whose polarization is directed by the nitrogen atom, participating in the double bond, and the electrophilic aromatic nucleus increases the polarization.



The $\pi$p$\pi$-conjugated system is also found in 2-methylenedihydroindole and N-vinylcarbazole, which were studied polarographically by F. Ender et al. [49], though in these cases the multiple bonds were purely carbon ones. The absence of a second nitrogen atom in aryl-N-vinyls decreases the conjugation activity: according to our measurements [40] with a dropping mercury electrode, arylhydrazones were reduced at 1.08 v, while under the same conditions 1-methylenedihydroindole and N-vinylcarbazole gave a wave at 1.30 v. The difference of 0.22 v in the potentials corresponds to 10.1 kcal/mole of energy, which is a quantitative measure of the nitrogen atoms' activating effect on the bond in arylhydrazones. The activation energy of bonds in hydrazone $\pi$p$\pi$-systems is about 18 kcal/mole less than in the azoform of $\pi\pi$-systems [40].

The enehydrazine form of arylhydrazones has a system of two multiple bonds, one of which is aromatic, separated by two nitrogen atoms $>\overset{1}{C}{=}\underset{|}{\overset{2}{C}}{-}\underset{|}{\overset{3}{\ddot{N}}}{-}\underset{|}{\overset{4}{\ddot{N}}}{-}\underset{|}{\overset{5}{C}}{=}\overset{6}{C}<$.

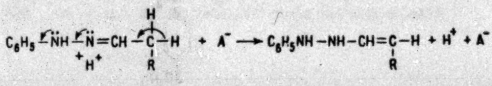
Each double bond reacts with the unshared electrons of the adjacent nitrogen atom, i. e., there are here two groups with $\pi$p-conjugation. The free electron pairs of the nitrogen atoms doubtlessly react with each other and affect the nature of the N−N bond, joining the $\pi$p-groups into one $\pi$pp$\pi$-conjugated system. This 1,6-system is less polar than the hydrazone $\pi$p$\pi$-system as it has a symmetrical structure. The $\pi$pp$\pi$-system has some polarity, firstly, due to the fact that one double bond is in the electrophilic aromatic nucleus, which destroys the symmetry and gives a polarization direction when treated with reagents; secondly, the hyperconjugation of the carbonyl radical also acts in the same way



$$>\overset{1}{C}=\overset{2}{C}-\overset{3}{N}-\overset{4}{N}-\overset{5}{C}=\overset{6}{C}-\overset{H}{C}-H\ .$$

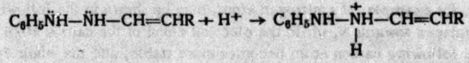
Thus, enehydrazine molecules contain a πppπ-conjugated system in which the 1st and 6th atoms are most reactive. The bond activation energy in this system is, according to our measurements [40], approximately 15 kcal/mole less than in the hydrazone πpπ-system.

We shall now examine the effect of medium on the state of the tautomeric equilibrium of arylhydrazones. As arylhydrazones are compounds with a basic character, an acid medium would have the greatest effect on them. For example, an aldehyde phenylhydrazone, which has a hydrazone structure, can react with an acid in the 1,4-position of the πσ-system



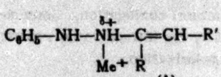
$$C_6H_5-\ddot{N}H-\underset{+H^+}{\ddot{N}}=CH-\underset{R}{\overset{H}{C}}-H + A^- \longrightarrow C_6H_5NH-NH-CH=\underset{R}{C}-H + H^+ + A^-$$

and be converted into an enehydrazine, i. e., into a more basic compound. In an acid medium a ketone enehydrazine formed or an arylhydrazone adds a proton to the more nucleophilic nitrogen atom



$$C_6H_5\ddot{N}H-\ddot{N}H-CH=CHR + H^+ \rightarrow C_6H_5NH-\underset{\overset{|}{H}}{\overset{+}{N}H}-CH=CHR$$

and becomes a cation, in which the ethylene bond is strongly polarized, i. e., dienophilic. The $\ddot{N}-\overset{+}{\ddot{N}}$ bond also becomes polar. The formation of a complex (A) also leads to the same effect.



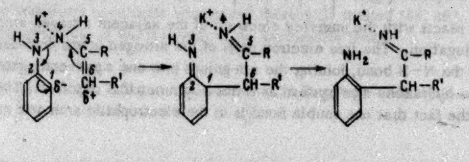
$$C_6H_5-NH-\underset{\overset{|}{Me^+}}{\overset{\delta+}{NH}}-\underset{\overset{|}{R}}{C}=CH-R'$$

(A)

Thus it is possible to understand the effect of catalysts in the Fischer reaction, as they are acidic reagents and compounds capable of forming complexes; they displace the tautomeric equilibrium of arylhydrazones towards the enehydrazine form and activate the bonds in it.

The most characteristic property of 1,4-conjugated systems is their capacity to participate in diene synthesis reactions. We consider that some 1,6-conjugated systems are capable, under specific conditions, of redistributing electron densities with intramolecular conversion of the diene synthesis type.

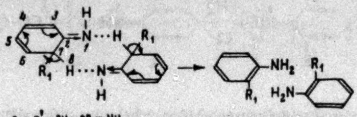
We showed above that in an acid medium or by complex formation, the enehydrazine forms of arylhydrazones were activated — a dieneophilic ethylene bond appears in them, the rest of the πppπ-conjugated system is also polarized and as a result atoms 1 and 6 acquire some excess charges which are opposite in sign. If one considers that these atoms are spatially close, then their attraction appears wholly probable and without doubt, would lead to redistribution of electron densities in the system by the following scheme



The analogy between this conversion and the reaction of diene synthesis is complete. Atoms 1, 2, 3, and 4 form a diene system – the 1, 2 ($\pi$)-multiple bond is conjugated with the free electron pairs of the 3rd and 4th atoms (pp) (such a conjugation should be similar in many ways to $\pi\pi$-conjugation) and the conjugation is strengthened by a coordination $K^+ \ldots N$ bond. The reaction of diene synthesis is characterized by the formation of a multiple bond between the 2nd and 3rd atoms and new bonds between the dieneophil and the 1st and 4th diene atoms with breaking of 1–2 and 3–4 bonds. All this also occurs in the scheme given above. Under the conditions of a Fischer reaction the o-iminoalkylquinonimine, formed as a result of the reaction, would, of course, rearrange itself into an o-iminoalkylaniline, which would finally give an indole, as the Robinson scheme shows. Thus, the general theory of conjugation allowed us to find "the moving force" of the conversion occurring in a Fischer reaction.

Comparing our ideas with the Robinson scheme, we see that there is an extra stage in their mechanism as we consider that o-iminoalkylaniline is formed directly, omitting the diamine stage. Furthermore, in the case of aliphatic and alicyclic ketones, the tautomeric conversion stage is also absent in the reaction, as we proved their enehydrazine structure.

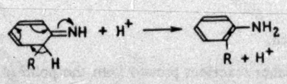
There remains to be clarified the mechanism of the conversion from o-iminoquinone to o-alkylaniline, i. e., the mechanism of the conversion from a quinoid to a benzene structure. It is hard to imagine why a hydrogen atom should move into the ortho- or, even more so, into the para-position in the molecule. We shall try to elucidate what bond reactions there are in an o-quinonimine molecule, formed as a result of arylhydrazone rearrangement in the first stage of a Fischer reaction. Here the polar C=N bond is conjugated with two double bonds of the ring and with the C–H bond, and all this $\pi\pi\pi\sigma$-system is polarized, and due to this the C–H bond is weakened, while a high electron density arises on the nitrogen atom.



$R_1 = R'-CH-CR=NH$

The orientation of the polar molecules and their drawing together leads to a redistribution of electron densities, for which, as we know, conjugated systems have a tendency.

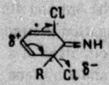
However, if the reaction is carried out in dilute acids, then the proton of the medium participates in the conversion.



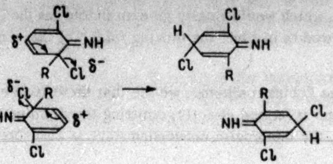
The conversion from the quinoid to the aromatic structure consists of this very 1,8-addition, which occurs with the transfer of the reaction center.

R. B. Carlin and E. E. Fisher [30, 50] found that 5,7-dichlorindoles were formed from 2,6-dichlorophenylhydrazones by the Fischer reaction, but they could not explain the mechanism of the migration of chlorine during the reaction. They succeeded [50] in establishing that the migration was completed intramolecularly and therefore the authors considered that the chlorine atom in an "electropositive" state formed an intermediate $\pi$-complex and migrated, without leaving the valence atmosphere of the aromatic ring, i. e., the obscure was explained by the unknown, as the $\pi$-complex was thought up by M. J. S. Dewar [51] for the explanation of certain reactions, but their existence was not proved.

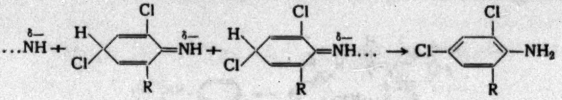
In order to clarify this problem, let us examine the reaction of bonds in the quinone, formed from 2,6-dichlorophenylhydrazone. In it the polar C–Cl bond is conjugated with the adjacent multiple bond ($\pi\sigma$).



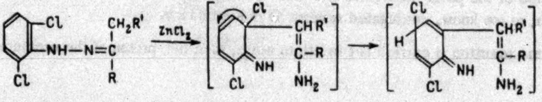
**The second chlorine atom, connected directly to the double bond, acts in a direction contrary to the conjugation and disconnects this bond from the conjugation chain; due to the opposite polarization, the C−N bond also resists conjugation with the C−Cl bond. The reaction of o-quinone molecules, similar to that described above, results in an exchange of chlorine atoms and the formation of a p-quinoid structure.**



**ππσ-Conjugation occurs in p-quinone which weakens the C−H bond and increases the nucleophilicity of the nitrogen atom. The C−H bond is also weakened by the effect of the electronegative chlorine, situated at the same carbon atom. The polar molecules exchange hydrogen atoms by reacting in pairs or, what is more likely, by a chain mechanism and are converted into aromatic amines.**

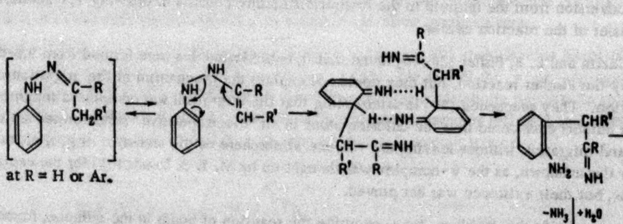


**Thus, the chlorine atom moves to the meta-position, while the amine formed would then give 5,7-dichlorindole. In a private paper to P. Carlin [50], F. Sidgwick proposed the following description for the chlorine migration**

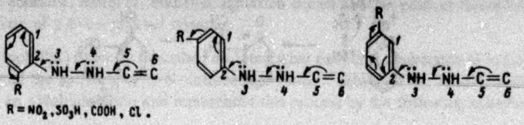


**but he could not explain this conversion.**

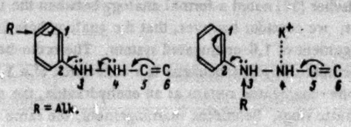
**Thus, the mechanism of the Fischer reaction, proved from the point of view of the general theory of conjugation and defined more accurately by us, may be represented by the following scheme**



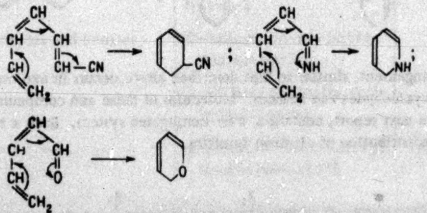
Such an explanation of the mechanism of the Fischer reaction is in agreement with all experimental facts. The absence of para-rearrangement products is explained by the reaction of the spatially close 1st and 6th atoms of the conjugated system and not the 1st and 8th atoms, which are further apart, while further conversion in the system, after rearrangement, stops with the closure of the pyrrole ring. The effect of substituents in the arylhydrazone nuclei on the course of the reaction was very thoroughly investigated by V. V. Feofilaktov [41], as has been mentioned before. Electrophilic substituents hinder the reaction as due to their effect the electron density on the first atom of the conjugated system decreases and this decreases the probability of the formation of an enehydrazine, which, apparently, does not form at all for dinitrophenylhydrazones. As may be expected, an ortho-substituent has the greatest effect, a para- somewhat less and a meta-substituted the least.



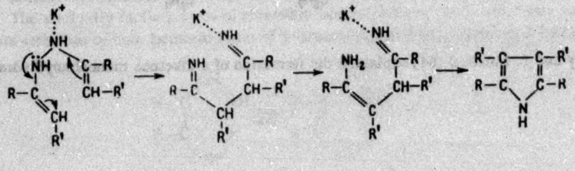
Nucleophilic substituents, on the contrary, somewhat increase the electron density at the first atom, i. e., facilitate rearrangement. Secondary alkylarylhydrazones are more readily converted into indoles than arylhydrazones, as the alkyl increases the polarity of the system and strengthens the conjugation of the 1–2 and 3–4 bonds.

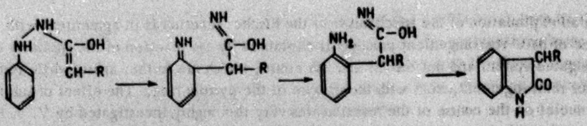


One should not think that the rearrangement of the diene synthesis type examined above is an exceptional phenomenon. Regrettably, π-conjugated 1,6-systems have been little studied and we were unable to find in the literature examples of similar conversions of them. It appears to us that rearrangements are possible, for example, in the following cases

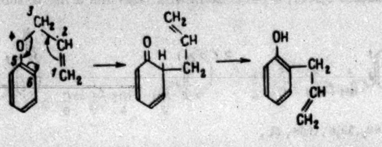


On the contrary, intramolecular conversions of the diene synthesis type are known for certain πppπ- and πpσπ-systems. For example, the synthesis of pyrroles from azines and oxindoles from 1-acyl-2-arylhydrazines, as in other cases of Fischer reactions, include such a rearrangement



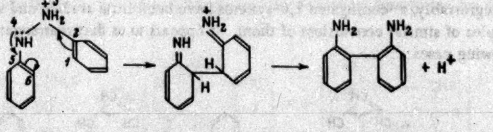


The Claisen rearrangement is a case of conversion in a $\pi p \sigma \pi$-system

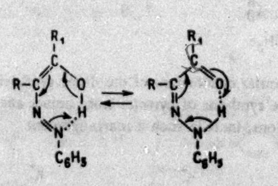


The rearrangement mechanism has been thoroughly studied and all its stages have been experimentally confirmed. It was found that ortho- precedes para-rearrangement [52, 53]. Using the Claisen rearrangement as an example one can see that a thorough chemical study of a reaction sometimes makes it possible to clarify the intermediate stages, but the nature of the mechanism may still remain unclear.

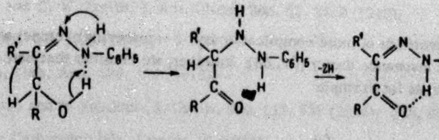
R. B. Carlin and E. E. Fischer [30] noted a formal analogy between the first stage of the Fischer reaction and the Claisen rearrangement; we consider however, that the analogy here is in principle — both processes are particular cases of the rearrangement of 1,6-conjugated system. The ortho-benzidine rearrangement is also of this type, while para-rearrangement of hydrazobenzene is a conversion of a 1,10-conjugated system. Hydrazobenzene contains the same $\pi p p \pi$-conjugated system as an enehydrazine, the only difference being that in this case both $\pi$-bonds are in aromatic rings. Benzidine rearrangement, the same as the Fischer reaction, occurs in the presence of acids



Apparently rearrangement, similar to that described above, occurs in azo compounds obtained from phenylhydrazones of $\alpha$-hydroxyaldehydes and ketones. Molecules of these azo compounds, whose formation mechanism will be examined in the next report, contain a $\pi \pi \sigma$-conjugated system. Such a system, in all probability, is capable of reversible redistribution of electron densities.

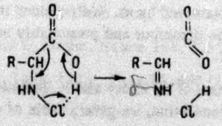


V. Barry and P. Mitchell [54] explained the formation of a diketone monophenylhydrazone in the following way



i. e., they assumed the simultaneous transfer of three hydrogen atoms and then the loss of two of them, which is very improbable. We consider, however, that first oxidation occurs and the product formed undergoes a rearrangement, characteristic of 1,6-conjugated systems.

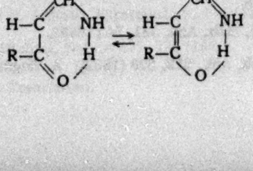
S. Fox and M. Bullock [55] recently described an interesting case of a conversion of a 1,6-conjugated system. The authors observed the splitting of α-N-chloroaminoglutaric acid with the formation of hydrogen chloride, carbon dioxide and an aldehydeimine and represented this process by the following scheme



| Nitrogen-containing compound | Carbonyl compound | Possible products of catalytic decomposition | Remarks |
|---|---|---|---|
| Hydrazine | Aldehydes and ketones, carboxylic acids | Substituted pyrroles, oxazolines, pyrrolinones-2 | Piloty reaction |
| Arylhydrazine | Aldehydes and ketones, carboxylic acids | Indoles, oxindoles, benzoxazolines | Fischer reaction, Brunner reaction |
| Semicarbazide | Aldehydes and ketones | 2-Aminooxazoles, imidazolones-2 | – |
| Thiosemicarbazide | Aldehydes and ketones | 2-Aminothiazoles, imidothiazolones-2 | – |
| Arylsemicarbazide | – | 2-Aminoaryloxazoles, arylimidazolones-2 | – |
| Arylthiosemicarbazide | – | 2-Aminoarylthiazoles, arylimidothiazolones-2 | Fischer reaction |

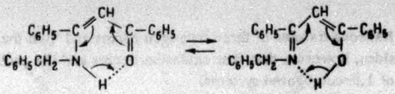
One can readily be convinced that this reaction is a conversion of the diene synthesis type in a σσσ-system.

Examples of tautomeric conversions are also known which proceed by the mechanism of the rearrangement of a 1,6-conjugated system. N. K. Kochetkov and Ya. Dombrovsky [56] recently published a paper on the tautomerism of alkyl β-aminovinyl ketones. The authors concluded that these compounds were a mixture of enamino- and amido-forms. The unusually facile process of reversible isomerization of both forms they were inclined to explain by a chelate structure of both isomeric forms of β-aminovinyl ketones, including a hydrogen bond



In other words, in this case we have an example of a reversible rearrangement of a ππp-conjugated system.

Previously, similar conversions of more complicated aryl β-aminovinyl ketones were studied and explained from the point of view of the resonance theory [57, 58]; however, we consider that here too rearrangement of a 1,6-conjugated system occurs, as for example



Apparently, tautomeric conversions of monohydrochlorides of diiminomalonates have the same mechanism [59].

The examples given here far from exhaust the analogy. The future will show how widespread in organic chemistry are rearrangements, like those examined by us. We consider it noteworthy that the general theory of conjugation makes is possible to connect the numerous and presumably separate facts, which make the study and exposition of organic chemistry so difficult.

Thus, the Fischer reaction and syntheses of O. Piloty and K. Brunner are particular cases of 1,6-conversions, namely of πppπ-conjugated systems. In conclusion, we give a table of compounds which, we consider, may undergo such rearrangements, and their possible conversion products.

As the data in the table show, many reactions have not yet been studied and if they can be carried out, our ideas will be fully confirmed.

## LITERATURE CITED

[1] E. Fischer and F. Jourdan, Ber. 16, 2241 (1883).

[2] E. Fischer and O. Hess, Ber. 17, 559 (1884).

[3] E. Fischer, Ber. 19, 1563 (1886).

[4] E. Fischer, Lieb. Ann. 236, 116 (1886).

[5] A. E. Arbuzov and V. M. Tikhvinsky, J. Russ. Chem. Soc. 45, 69 (1913).

[6] A. E. Arbuzov and V. M. Tikhvinsky, Ber. 43, 2301 (1910); J. Russ. Chem. Soc. 45, 70 (1913).

[7] A. E. Arbuzov and A. P. Friauf, J. Russ. Chem. Soc. 45, 694 (1913).

[8] A. E. Arbuzov and N. E. Khrutsky, J. Russ. Chem. Soc. 45, 699 (1913).

[9] A. E. Arbuzov and R. E. Vagner, J. Russ. Chem. Soc. 45, 1697 (1913).

[10] A. E. Arbuzov and V. A. Rotermel, J. Gen. Chem. 2, 397 (1932).

[11] A. E. Arbuzov and I. A. Zaitsev, Trans. Kazan Inst. Chem. Tech. 1, 33 (1934).

[12] A. E. Arbuzov, I. A. Zaitsev, and A. I. Razumov, J. Gen. Chem. 6, 289 (1936).

[13] K. Brunner, Monatsh. 17, 267, 1479 (1896).

[14] W. Borsche, Lieb. Ann. 359, 52 (1908).

[15] W. H. Perkins and S. G. P. Plant, J. Chem. Soc. 125, 1503 (1924).

[16] O. Piloty, Ber. 43, 497 (1910).

[17] Treibs, Steiner, and Kirchhof, Lieb. Ann. 581, 54 (1953).

[18] E. Fischer and E. Bestorn, Lieb. Ann. 212, 326 (1882); A. Hugershoff, Ber. 36, 3134 (1903).

[19] W. H. Perkin and Titley, J. Chem. Soc. 121, 1568 (1922).

[20] H. R. Snyder and C. W. Smith, J. Am. Chem. Soc. 65, 2452 (1943).

[21] K. Brunner, Ber. 31, 1954 (1898).

[22] G. Reddelien, Lieb. Ann. 388, 179 (1912).

[23] G. M. Robinson and R. Robinson, J. Chem. Soc. 113, 639 (1918); 125, 827 (1924).

[24] G. Cohn, Die Carbazolgruppe, Leipzig 12 (1919).

[25] C. Hollins, J. Am. Chem. Soc. 44, 1599 (1923).

[26] S. Bodforss, Ber. 58, 755 (1925).

[27] P. W. Neber, G. Knoller et al., Lieb. Ann. 471, 113 (1929).

[28] C. F. N. Allon and C. V. Wilson, J. Am. Chem. Soc. 65, 611 (1943).

[29] K. H. Pausacker and C. J. Schubert, Nature 163, 289 (1949); J. Chem. Soc. 1949, 1384.

[30] R. B. Carlin and E. E. Fisher, J. Am. Chem. Soc. 70, 3421 (1948).

[31] P. N. Gore, G. K. Hughes, and E. Ritche, Nature 164, 835 (1949).

[32] K. Clusius and H. R. Weisser, Helv. Chim. Acta 35, 400 (1952).

[33] R. Nietzki and O. Goll, Ber. 18, 3552 (1855).

[34] H. Plieninger, Ber. 83, 273 (1950).

[35] H. Plieninger and J. Nogrādi, Ber. 88, 1964 (1955).

[36] C. S. Barnes and K. H. Pausacker, J. Chem. Soc. 1951, 730.

[37] G. Plancher, Ber. 31, 1496 (1898).

[38] A. Reissert and H. Heller, Ber. 37, 4378 (1904).

[39] G. Jenisch, Monatsh. 27, 223 (1906).

[40] A. E. Arbuzov and Yu. P. Kitaev, Proc. Acad. Sci. USSR 113, 577 (1957).*

[41] V. V. Feofilaktov and N. K. Semenova, J. Gen. Chem. 23, 644 (1953).*

[42] W. Teilacker and O. R. Leichtle, Lieb. Ann. 572, 121 (1951).

[43] K. H. Pausacker and C. J. Schubert, J. Chem. Soc. 1950, 1814.

[44] J. McLean, S. McLean, and R. J. Reed, J. Chem. Soc. 1955, 2519.

[45] A. N. Nesmeyanov, Sci. Reports, Moscow State Univ. 132, 5 (1950).

[46] A. Nesmeyanov and M. I. Kabachnik, J. Gen. Chem. 25, 56 (1955).*

[47] A. Remick, Electronic Concepts in Organic Chemistry, For. Lit. Press, 1950, 489 [Russian translation].

[48] F. Ender, Z. Elektroch. 54, 219 (1950).

[49] F. Ender, E. Tahrbwach, and H. J. Teuber, Angew. Chem. 66, 293 (1954).

[50] R. B. Carlin, J. G. Wallace, and E. E. Fisher, J. Am. Chem. Soc. 74, 990 (1952).

[51] M. J. S. Dewar, The Electronic Theory of Organic Chemistry, Oxford 18, 143, 193, 212 (1949).

[52] C. D. Hurd and M. A. Pollack, J. Org. Chem. 3, 550 (1939).

[53] K. Schmid, W. Halgel, and H. Schmid, Experientia 9, 414 (1953); Ch. A. 49, 1625 (1955).

[54] V. C. Barry and P. W. D. Mitchell, Nature 175, 220 (1955).

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* Original Russian pagination. See C.B. Translation.

[55] S. W. Fox and M. W. Bullock, J. Am. Chem. Soc. 73, 2754 (1951).

[56] N. K. Kochetkov and Ya. Dombrovsky, J. Gen. Chem. 26, 3081 (1956).*

[57] N. H. Cromwell and W. R. Watson, J. Org. Chem. 14, 411 (1949).

[58] J. B. Culbertson, J. Am. Chem. Soc. 73, 4818 (1951).

[59] S. M. McElvain and B. E. Tate, J. Am. Chem. Soc. 73, 2760 (1951).

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* Original Russian pagination. See C.B. Translation.

# SYNTHESES OF HETEROCYCLIC COMPOUNDS BASED ON THE FISCHER REACTION

## II. THE ANOMALOUS COURSE OF THE FISCHER REACTION

A. E. Arbuzov and Yu. P. Kitaev

An anomalous Fischer reaction was discovered by one of us in 1913. It was first observed in catalytic decomposition of aldehyde phenylhydrazones in the presence of cuprous chloride [1], when the former underwent nitrile decomposition. A detailed investigation of this reaction showed that aldehyde phenylhydrazones with large radicals form, almost exclusively, nitriles and aniline while lower aldehydes also give indole. It was then also discovered that acetone phenylhydrazone underwent catalytic decomposition in the presence of cuprous chloride not to form 2-methylindole, but a new compound, ammonia and aniline. This observation and a series of other unpublished facts suggested the hypothesis that ketone phenylhydrazones, not containing a $CH_2$ group next to the carbonyl group, would also decompose anomalously under these conditions.

In 1950 O. M. Shapshinskaya [2] attempted to study the anomalous reaction of the catalytic decomposition of acetone phenylhydrazone in detail. She isolated two fractions from the reaction mixture, one of which was found to be aniline. The second fraction boiled at 267-269° (d 1.054). The substance in this fraction did not dissolve in water, but dissolved in dilute (1:1) hydrochloric acid; hydrolysis of it gave acetone. According to analytical data, the compound obtained had the composition $C_6H_7N$, but considering the high boiling point, the authors consider that this formula should be doubled. The anomalous decomposition of acetone phenylhydrazone may then be illustrated by the overall equation

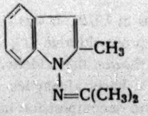
$$2C_9H_{12}N_2 \longrightarrow C_6H_5NH_2 + NH_3 + C_{12}H_{14}N_2$$

The authors were unable to elucidate the structure of the anomalous product.

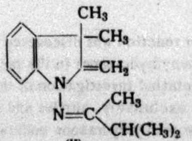
We decided to check, first of all, if the phenylhydrazones of all ketones, which do not contain a methylene group next to the carbonyl group, would actually undergo an anomalous Fischer reaction in the presence of cuprous chloride. For this purpose we studied the decomposition of phenylhydrazones of acetone, methyl isopropyl ketone, pinacolin, pyruvic acid, ethyl pyruvate, acetophenone, p-chloroacetophenone and acetone methylphenylhydrazone. The anomalous reaction products were isolated only in the case of the phenylhydrazones of acetone and methyl isopropyl ketone. The amount of ammonia evolved in these cases corresponded to the above reaction scheme. Of the other phenylhydrazones that we investigated, their decomposition gave considerably less ammonia than that required by the equation of the normal reaction, but sometimes somewhat more than what should have been evolved in an anomalous reaction. From the tars formed from the phenylhydrazones of acetophenone, p-chloroacetophenone and ethyl pyruvate we were able to isolate the normal catalytic decomposition products – indoles – in the first two cases in insignificant amounts and in the last, in a yield of 19.1%. On heating acetone methylphenylhydrazone to 250° with cuprous chloride, very small amounts of ammonia were evolved and the reaction mixture became tarry. The tar contained the starting hydrazone and lower boiling decomposition products.

Several repetitions of the experiments, the use of solvents (kerosene, nitrobenzene, dimethylaniline, etc.) as well as fractionation under high vacuum, chromatography on silica gel and aluminum oxide and the use of selective solution in working over the tars obtained did not result in the separation of individual compounds. Apparently, due to the high temperatures during the reaction, the anomalous products were decomposed; we therefore stopped working in this direction and then set out to clarify the structure of the compounds obtained from the phenylhydrazones of acetone and methyl isopropyl ketone.

Hydrolysis of the anomalous products with dilute sulfuric acid gave acetone and methyl isopropyl ketone; the former was detected by reaction with salicylaldehyde and from the latter we obtained a dinitrophenylhydrazone. We established the presence of three labile hydrogen atoms, corresponding to the 2-methyl group of indole, in a molecule of the compound, prepared from acetone phenylhydrazone. As we could not obtain an anomalous product by the catalytic decomposition of acetone methylphenylhydrazone in the presence of cuprous chloride, we concluded that the product was an N-substituted indole. This was also supported by the fact that regardless of the high boiling point the substance did not crystallize even when cooled to −70° and it is known that all N-substituted indoles of the corresponding molecular weight are high boiling, noncrystallizing liquids [3]. Considering the above observations, we assigned the compounds obtained the structure of acetone 2-methylindol-1-aminide (I) and methyl isopropyl ketone 3,3-dimethyl-2-methylenindolin-1-aminide (II).



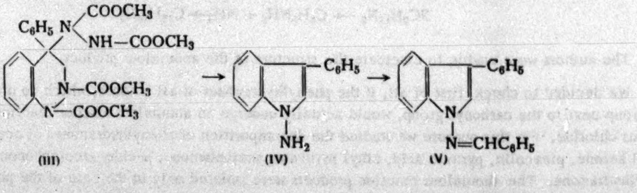
(I)



(II)

Both compounds were yellow liquids, reddening rapidly in air and readily soluble in dilute acids and organic solvents; they did not give a reaction for indole with a pine splinter. Nitrogen analysis in both cases gave results that agreed with the proposed reaction formulas. The yield was 21-41% of (I) and 12% of (II). It should be noted that in different experiments the yields of acetone 2-methylindol-1-aminide (I) varied greatly and it could not be isolated at times. Apparently, this was due to the varying purity of the catalyst.

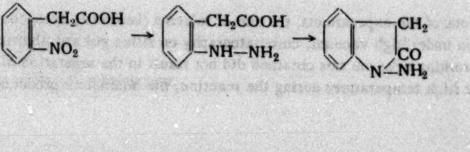
Recently K. Alder and H. Niklas [4] obtained a derivative of N-aminoindole for the first time. The authors were studying the reaction of substituted styrene with azodicarboxylic esters. From α-phenylstyrene and two molecules of ester they obtained compound (III), which belongs to the tetrahydrocinnoline series.



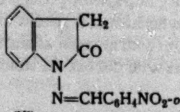
(III) (IV) (V)

Treatment of this compound with hydrazine hydrate gave a good yield of 3-phenyl-N-aminoindole (IV) (m. p. 104°), which was a colorless crystalline material, readily oxidized and becoming yellow. The amino group in this compound had hydrazine properties; thus, K. Alder and H. Niklas treated it with benzaldehyde to obtain N-benzalimino-3-phenylindole (V), whose melting point (108°) hardly differed from the melting point of the starting amine. Compound (V) was similarly prepared by us as an anomalous Fischer reaction product.

Considerably earlier P. Neber et al. [5, 6] and A. Kliegel [7] prepared N-aminooxindole by the following reaction



In the given case the amino group also had a hydrazine character; with o-nitrobenzaldehyde it gave compound (VI).

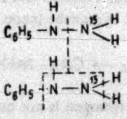


(VI)

Consequently, in order to prove the structure of the products obtained by us conclusively, we may use one of these methods for their synthesis. Furthermore, it was necessary to try to isolate 1-aminoindoles by hydrolysis of the anomalous products since, on the one hand, this would also prove the structure of the latter and, on the other, would make it possible to study the properties of the former compounds, which up to now have been poorly accessible.

After establishing the structure of the anomalous products it was necessary to elucidate their formation mechanism. We started with the assumption that the formation of nitriles from aldehyde arylhydrazones and anomalous products from ketone arylhydrazones proceeded by the same mechanism.

One of us found [8] that heating to 150° with cuprous chloride caused the decomposition of phenylhydrazine with the evolution of nitrogen, ammonia and aniline. Even earlier, Struthers [9] observed the decomposition of phenylhydrazine in the presence of mercury or copper cyanide and, besides the products mentioned, he also isolated benzene. It seemed to us that this process might be connected with the anomalous course of the Fischer reaction. We shall not mention here all the information on other substances which cause this decomposition of arylhydrazones, but shall only examine the report by K. Clusius [10], who studied the catalytic decomposition of phenylhydrazine labeled with the isotope $N^{15}$, using cuprous chloride. The author synthesized $C_6H_5NH \cdot N^{15}H_2$ and, having decomposed it in a special apparatus, isolated nitrogen, ammonia, benzene and aniline in a pure state. All nitrogen-containing products were decomposed and the nitrogen obtained from them analyzed for isotope content. It must be noted that all the work was carried out with 0.6 g of the substance, but with great accuracy. The results of the isotopic analysis are given in Table 1 and show that the nitrogen atoms labeled with the isotope $N^{15}$ passed quantitatively into ammonia, half into nitrogen, and were completely absent from aniline; this process K. Clusius illustrated by the scheme



According to Clusius, one phenylhydrazine molecule loses nitrogen and hydrogenates its own phenyl and a second molecule with the elimination of the amino group.

TABLE 1

| Substances | | Average N15 content (in at. %) | |
|---|---|---|---|
| | | found | calculated |
| Starting | 1) $N^{15}H_4Cl — NaN^{15}O_2$ | 4.86 | |
| | 2) phenylhydrazine | 2.58 | $2.62 = \frac{0.38^{*} + 4.86}{2}$ |
| Reaction products | 3) nitrogen | 2.56 | 2.58 |
| | 4) ammonia | 4.79 | $4.78 = 2 \cdot 2.58 - 0.38^{*}$ |
| | 5) aniline | 0.39 | $0.38^{*}$ |

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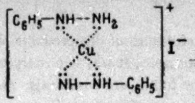
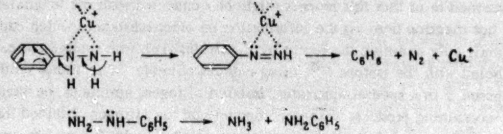
• N15 content in normal nitrogen.

On the basis of the ideas of the general theory of conjugation, we proposed the following explanation for the mechanism of the catalytic decomposition of phenylhydrazine. The catalyst forms a complex with phenylhydrazine; for example, $C_6H_5NHNH_2 \cdot CuCN$ [9], $2C_6H_5NHNH_2 \cdot CuI$ [8], $2C_6H_5NHNH_2 \cdot ZnCl_2$ [11], etc. have been isolated. Consequently, some part of the phenylhydrazine is present in the reaction mass as a complex while the other part remains unchanged. In all probability both nitrogen atoms in the complex form a coordination bond with the metal, i. e., for example, the complex with CuI has the structure given below and is similar to the "chelate compounds."



In forming the coordination bond the metal attracts the unshared electron pairs from the nitrogen atoms and this causes a certain displacement of the electrons of the N−H bond toward nitrogen, i. e., these bonds are weakened. Furthermore, the N−H bonds are conjugated with the benzene ring bonds which makes the hydrogen atoms even more labile. In free phenylhydrazine the unshared electron pairs give to the nitrogen atoms a nucleophilic character, which includes the capacity of these atoms to form hydrogen bonds [12, 13]. The reaction of the complex compound and free phenylhydrazine, proceeding by the scheme



results in the formation of diazobenzene, ammonia and aniline. Due to the high temperature and the catalyst, the diazobenzene decomposes to nitrogen and benzene. The catalyst is thus freed and again forms a complex, and this causes further conversions.

This explanation agrees fully with Clusius' observations and shows the similarity between the decomposition of phenylhydrazine and the known reaction of hydrazobenzene disproportionation [14].

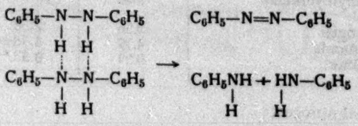
$$2C_6H_5{-}NH{-}NH{-}C_6H_5 \rightarrow C_6H_5{-}N{=}N{-}C_6H_5 + 2C_6H_5NH_2$$

In this case the azo compound is stable and nitrogen is not evolved.

Disproportionation is caused by heating or irradiating an alcoholic solution of the hydrazo compound with ultraviolet light. Recently, P. F. Holt and B. P. Hughes [13] investigated the thermal decomposition of hydrazobenzene, containing nitrogen labeled with a heavy isotope. The azobenzene obtained did not differ in isotope content from the starting hydrazobenzene which showed that during the reaction the N−N bond was not broken, but this contradicts the radical mechanism of disproportionation. In 1912 Wieland [16] proposed an intermolecular oxidation-reduction mechanism.

$$C_6H_5{-}NHNH{-}C_6H_5 \rightarrow C_6H_5N{=}NC_6H_5 + 2H; \quad C_6H_5{-}NHNH{-}C_6H_5 + 2H \rightarrow 2C_6H_5NH_2$$

On the basis of their experimental results, P. F. Holt and B. P. Hughes consider that disproportionation did occur either in accordance with Wieland's mechanism or by the scheme



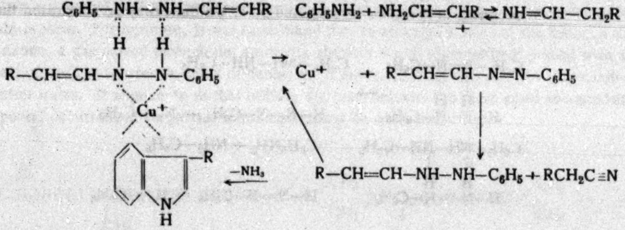
$$\begin{array}{ccc} C_6H_5{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{H}{|}}{N}{-}C_6H_5 & & C_6H_5{-}N{=}N{-}C_6H_5 \\ \vdots\quad\vdots & \longrightarrow & \\ C_6H_5{-}\underset{\underset{H}{|}}{N}{-}\underset{\underset{H}{|}}{N}{-}C_6H_5 & & C_6H_5NH + \underset{\underset{H}{|}}{H}N{-}C_6H_5 \end{array}$$

In order to prove the above scheme the authors made cryoscopic measurements and showed that association of hydrazobenzene molecules may actually occur.

One would expect that α,β-alkylphenylhydrazines are also capable of disproportionation to form amine, benzeneazoalkane and aniline. It is possible that the appearance of azo compounds and hydrazones observed by M. P. Grammaticakis [17] in alcoholic solutions of alkylphenylhydrazines is also due to this process and not to the oxidation of the hydrazine with aerobic oxygen.

It seems to us that the formation of nitriles and N-substituted indoles from arylhydrazones in the presence of cuprous chloride may be explained by using the same scheme which we had put forward above for the catalytic decomposition of phenylhydrazine and disproportionation of hydrazobenzene.

1.



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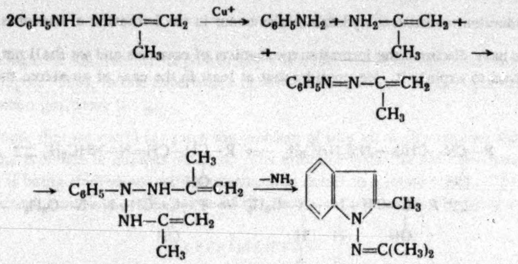
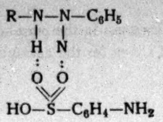


The details of these schemes should be studied and confirmed experimentally. However, we do not question the accuracy of such a mechanism.

We cannot yet prove why an anomalous Fischer reaction occurs in the presence of cuprous chloride and is not observed in the presence of zinc chloride, but maintain that it is due to the nature of the metal. Regrettably, the complexes of phenylhydrazine and phenylhydrazones have not yet been studied, but our assertions are based on the following. Firstly, zinc and copper chlorides behave differently in a Fischer reaction; secondly, the complexes of these salts with phenylhydrazine have a different reaction to heating: the zinc complex decomposes smoothly, while, as one of us noted earlier, the copper one decomposes with an explosion [8]. Apparently, both nitrogen atoms in the copper complex are under quite a strong influence from the complex-former, the zinc, however, either combines with only one nitrogen atom of the arylhydrazone, or else its effect on the nitrogen atom is less.

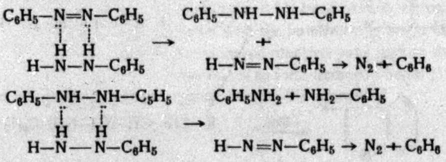
It is interesting to note that if cuprous chloride that had been stored for a long time was used for the reaction, no anomalous product could be isolated though neither was 2-methylindole formed if acetone phenylhydrazone was used.

We succeeded in finding another catalyst for the anomalous reaction in whose presence acetone phenylhydrazone gave the 2-methylindol-N-aminide of acetone (I) in a 70% yield and isovaleraldehyde phenylhydrazone gave the corresponding nitrile (42%). This catalyst is sulfanilic acid, which also catalyzes the decomposition of phenylhydrazine [18] to nitrogen, ammonia, aniline and benzene. In all probability, sulfanilic acid forms hydrogen bonds with the hydrazine or enehydrazine, i. e., in this case the free base would be the reducing agent.



Thus, the common catalysts of the two analogous processes seem to us to give further proof of their common mechanism.

Interesting observations, confirming our mechanism, are contained in the paper by P. Walther [19]. In particular, the author found that heating azobenzene with phenylhydrazine gave hydrazobenzene, nitrogen and benzene, and that, in its turn, hydrazobenzene with phenylhydrazine gave aniline, nitrogen and benzene. The processes occurring in reactions investigated by P. Walther, may be illustrated thus

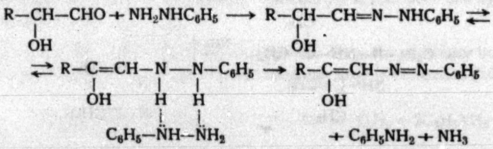


$$\begin{array}{lcl} C_6H_5-\ddot{N}=\ddot{N}-C_6H_5 & & C_6H_5-NH-NH-C_6H_5 \\ \qquad\;\; \vdots \quad \vdots & \longrightarrow & \qquad + \\ \qquad\;\; H \quad H & & \\ \quad H-N-N-C_6H_5 & & H-N=N-C_6H_5 \rightarrow N_2 + C_6H_6 \\ C_6H_5-\ddot{N}H-\ddot{N}H-C_5H_5 & & C_6H_5NH_2 + NH_2-C_6H_5 \\ \qquad\;\; \vdots \qquad \vdots & \longrightarrow & \\ \qquad\;\; H \qquad H & & \\ \quad H-N-N-C_6H_5 & & H-N=N-C_6H_5 \rightarrow N_2 + C_6H_6 \end{array}$$

The reaction of a hydroxyazo compound with phenylhydrazine has the same mechanism [20].

Oxidation-reduction reactions of hydrazines also occur in the formation of osazones.

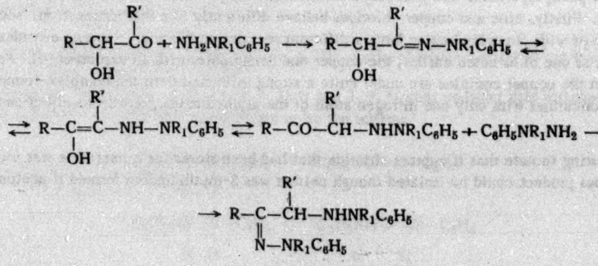
Many authors have discussed the formation mechanism of osazones and we shall not repeat here the various hypotheses put forward to explain it. We consider that at least in the case of an aldose the reaction proceeds in the following way



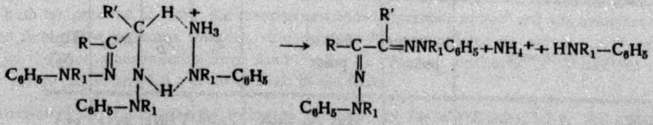
$$\begin{array}{l} R-\underset{\displaystyle OH}{\underset{|}{CH}}-CHO + NH_2NHC_6H_5 \longrightarrow R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH=N-NHC_6H_5 \rightleftarrows \\ \rightleftarrows R-\underset{\displaystyle OH}{\underset{|}{C}}=CH-\underset{\displaystyle \vdots}{\underset{\displaystyle H}{\underset{|}{N}}}-\underset{\displaystyle \vdots}{\underset{\displaystyle H}{\underset{|}{N}}}-C_6H_5 \longrightarrow R-\underset{\displaystyle OH}{\underset{|}{C}}=CH-N=N-C_6H_5 \\ \qquad\qquad\quad C_6H_5-\ddot{N}H-\ddot{N}H_2 \qquad\qquad\qquad\qquad + C_6H_5NH_2 + NH_3 \end{array}$$

We have already mentioned the further conversion of intermediate azo compound in discussing the mechanism of the Fischer reaction [15].

It is possible that ketoses react in the same way with phenylhydrazine, and according to G. Bloink and K. Pausacker's scheme [21], with methylphenylhydrazine.

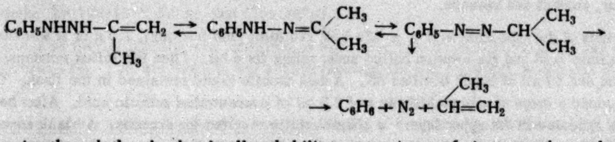


$$\begin{array}{l} R-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle R'}{\overset{|}{CO}} + NH_2NR_1C_6H_5 \longrightarrow R-\underset{\displaystyle OH}{\underset{|}{CH}}-\overset{\displaystyle R'}{\overset{|}{C}}=N-NR_1C_6H_5 \rightleftarrows \\ \rightleftarrows R-\underset{\displaystyle OH}{\underset{|}{C}}=\overset{\displaystyle R'}{\overset{|}{C}}-NH-NR_1C_6H_5 \rightleftarrows R-CO-\overset{\displaystyle R'}{\overset{|}{CH}}-NHNR_1C_6H_5 + C_6H_5NR_1NH_2 \longrightarrow \\ \longrightarrow R-\underset{\displaystyle N-NR_1C_6H_5}{\underset{\|}{C}}-\overset{\displaystyle R'}{\overset{|}{CH}}-NHNR_1C_6H_5 \end{array}$$



Consequently, the statement by G. Reddelien [11] on the mechanism of the catalytic decomposition of phenylhydrazine is not without basis, but he was incorrect in assuming that the complex was the oxidant.

We also found that in the catalytic decomposition of acetone phenylhydrazone in the presence of $ZnCl_2$ and $NiCl_2$ a certain amount of aniline was always formed, i. e., apparently in these cases an anomalous reaction occurred as a side process. Furthermore, it was established that in all cases studied of the decomposition of acetone phenylhydrazone, a gas passed through the ammonia absorber which when ignited, burned with a smoky flame. The smell of the gas was reminiscent of benzene. It decolorized an acid solution of potassium permanganate and bromine water. It appears to us that besides the main reaction, in these cases decomposition of a mixed azo compound occurred, as its partial formation cannot be excluded,



$$C_6H_5NHNH-\underset{\displaystyle CH_3}{C}=CH_2 \rightleftarrows C_6H_5NH-N=C\begin{matrix}CH_3\\CH_3\end{matrix} \rightleftarrows \underset{\downarrow}{C_6H_5}-N=N-CH\begin{matrix}CH_3\\CH_3\end{matrix} \longrightarrow$$

$$\longrightarrow C_6H_6 + N_2 + \overset{\displaystyle CH_3}{CH}=CH_2$$

i. e., the gas passing through the absorber in all probability was a mixture of nitrogen and propylene, possibly with traces of benzene vapor. Thus, in one experiment in decomposing 57 g of acetone phenylhydrazone, the losses, mainly of unabsorbed gas, were 2.5 g.

In conclusion we note that we could not solve the problem of why all arylhydrazones did not undergo the anomalous reaction in the presence of cuprous chloride. The effect of sulfanilic acid as a catalyst of the anomalous Fischer reaction is being studied and will be discussed in detail in a future report. The effect of a substituent in the phenylhydrazine nucleus on the course of the anomalous reaction is also being studied.

## EXPERIMENTAL

The hydrazones used in the work were prepared by the usual methods recommended in the literature and had the constants given in Table 2.

Decomposition of acetone phenylhydrazone in the presence of cuprous chloride. 25.5 g of hydrazone and 1.0 g of cuprous chloride were heated in an Arbuzov flask on a metal bath. The reaction began at 180° in the bath and proceeded for 35 min with a bath temperature of 260-270°. We trapped 1.3 g of ammonia (by the anomalous reaction scheme there should be 1.46 g and by the normal Fischer reaction – 2.93 g). A gas came through the ammonia absorber, which smelled of benzene and burnt with a smoky flame, on ignition. At 71°, several drops of a colorless liquid ($n_D^{20}$ 1.5010) fell into the receiver. During the reaction a yellow liquid (b. p. 182-185°) began to distill off. When ammonia was no longer evolved, the dark reaction mixture was distilled in vacuum to give a certain amount of a yellow liquid and a dark red tarry residue. The distillate was then separated into two fractions by distillation: 1st 68-75° (10mm), 7.8 g; 2nd 138-139° (10 mm), 3.3 g.

The first fraction was treated with acetic anhydride to give a solid substance with m. p. 112.5-113° (from water), which melted at 112°, when mixed with acetanilide, i. e., we had isolated aniline.

The 2nd fraction (yield 20.6%) had the following constants:

$d_4^{20}$ 1.0520, $n_D^{20}$ 1.5801, $MR_D$ 58.94, calculated 59.09. Found %: N 15.21, 15.12. $C_{12}H_{14}N_2$ (I). Calculated %: N 15.05.

TABLE 2

| Expt. No. | Phenylhydrazones | Melting point | Boiling point | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | Acetone | — | 128° (10 mm) | 1.0123 | 1.5865 | 49.15 | 83.2 |
| 2 | Methyl isopropyl ketone | — | 108.5 (0.5 mm) | 0.9751 | 1.5639 | 58.78 | 93.6 |
| 3 | Pinacolin | — | 147.9 (12 mm) | — | 1.5525 | — | — |
| 4 | Acetophenone | 104.5° | — | — | — | — | 98 |
| 5 | p-Chloroacetophenone | 113—114 | — | — | — | — | 94 |
| 6 | Pyruvic acid | 179—181 |  | — | — | — | 87.5 |
| 7 | Isovaleraldehyde | — | 115—116 (1.5 mm) | 0.9722 | 1.5611 | 58.74 | 92 |
| 8 | Ethyl pyruvate | 114—115 | — | — | — | — | — |
| 9 | Acetone methylphenylhydrazone | — | 116—117 (15mm) | — | 1.5578 | — | — |

The substance did not give an indole reaction with a pine splinter. It dissolved in dilute acids and also in acetone, ether, alcohol and benzene.

For hydrolysis of the substance with b. p. 138-139° (10 mm) (2nd fraction), 1.5 g of it was dissolved in 20 ml of 10% sulfuric acid and the solution boiled under reflux for 5 hrs. Then the reflux condenser was exchanged for a straight one and 12 ml of liquid distilled off. A dark mobile liquid remained in the flask. To 5 ml of the distillate were added 5 drops of salicylaldehyde and 2.5 ml of concentrated sulfuric acid. After heating, an orange red color appeared in the upper layer – a characterictic reaction for acetone. A blank experiment gave a yellow color; consequently, the substance contained the $-N=C(CH_3)_2$ group.

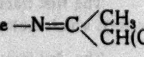
Determination of the active hydrogen by the Chugaev-Tserevitinov method showed that the substance contained three labile hydrogen atoms, corresponding to the $\alpha$-$CH_3$ group of indole.

Decomposition of methyl isopropyl ketone phenylhydrazone in the presence of cuprous chloride. 29.9 g of hydrazone and 0.8 g of catalyst were reacted. Decomposition began at a bath temperature of 210° and then proceeded at a bath temperature of 240-270°. We trapped 1.4 g of ammonia (for the anomalous reaction there should be 1.45 g). During the decomposition, a yellow liquid distilled off at 170-189°. A further small amount of yellow liquid came over during vacuum distillation of the dark reaction mixture, with b. p. 58-170° (13 mm) (decomp.).

Subsequent distillation of the liquid at 10 mm gave the following fractions: 1st 57-78°, a yellow liquid; 2nd 144-145°, 2.2 g, a bright yellow liquid; 3rd 148-155°, 1.3 g , a yellow liquid.

By treating it with acetic anhydride, we obtained acetanilide with m. p. 113° from the 1st fraction; the mixed melting point was 112-113°.

The substance of the 2nd fraction was insoluble in water, but dissolved in dilute sulfuric acid, acetone and alcohol. On standing in air, it became red.

For hydrolysis of the substance with b. p. 144-145° (10 mm) (2nd fraction), 0.95 g of it was dissolved in 15 ml of 10% $H_2SO_4$ and boiled under reflux for 4 hrs. Then 10 ml of liquid was distilled off and the distillate treated with an acid solution of dinitrophenylhydrazine. The precipitate was recrystallized from alcohol and melted at 117-118°. A mixture with methyl isopropyl ketone dinitrophenylhydrazone melted at 117°. Consequently, methyl isopropyl ketone was liberated on hydrolysis, i. e., the substance contained the  $-N=C\begin{cases}CH_3\\CH(CH_3)_2\end{cases}$ group.

Found %: N 11.73. $C_{15}H_{22}N_2$ (II). Calculated %: N 11.56.

*Decomposition of acetone phenylhydrazone in the presence of sulfanilic acid.* 33.0 g of hydrazone and 0.3 g of sulfanilic acid were heated in an Arbuzov flask on a Wood's metal bath. The evolution of ammonia began at a bath temperature of 200°; the reaction proceeded vigorously at 240° and was complete after 3.5 hrs. A gas passed through the ammonia absorber, which burnt with a smoky flame on ignition. We trapped 1.7 g of ammonia (for the anomalous reaction there should be 1.9 g). Vacuum distillation of the reaction mixture gave 24.2 g of a yellow liquid and 4.0 g of tar was left in the flask.

Distillation of the liquid gave the following fractions: 1st 72-78° (13 mm), 7.7 g; 2nd 130-135° (11 mm), 14.9 g; residue 1.4 g.

From the 1st fraction we isolated 7.2 g of aniline, which was identified as acetanilide. A second distillation of the 2nd fraction at 6 mm gave two fractions: 1st 120-130°, 0.8 g; 2nd 132-133°, 14.0 g; residue 0.1 g.

The 2nd fraction of the second distillation was the anomalous product and had the constants: $n_D^{20}$ 1.5808, $d_4^{20}$ 1.0532, close to those given above for substance (I). The yield was 70%; the same as the yield of aniline. The substance did not crystallize at −70° (cooling mixture: dry ice + ether).

*Decomposition of isovaleraldehyde phenylhydrazone in the presence of sulfanilic acid.* 25.7 g of hydrazone and 0.2 g of catalyst were reacted. Decomposition began when the bath temperature reached 200° and was complete after 1 hr at a bath temperature of 260°. The vapor temperature of the liquid distilling off was 170°. We trapped 0.1 g of ammonia. With slight decomposition, 16.0 g of a yellow liquid distilled off with b. p. 135-140° and 7.7 g of a dark red tar was left in the reaction flask. Subsequent distillation of the liquid obtained gave the following fractions: 1st 128-130°, 5.0 g; 2nd 178-186°, 7.1 g.

The substance of the 1st fraction was identified as isovaleronitrile by the boiling point and characteristic smell; the yield was 42%. The 2nd fraction was aniline (acetanilide was prepared), which was obtained in 53% yield.

*Decomposition of acetophenone phenylhydrazone.* 25.0 g of the phenylhydrazone and 0.8 g of cuprous chloride were heated in an Arbuzov flask on a Wood's metal bath in an atmosphere of $CO_2$. Evolution of ammonia began at 190° (in the bath) and was accompanied by the formation of a white deposit in the condenser – $(NH_4)_2CO_3$. The decomposition was complete after 1.5 hr at a bath temperature of 270°. We trapped 0.9 g of $NH_3$ (for the anomalous reaction 1.01 g should be liberated). The brown reaction mixture was distilled at 2 mm to give the following fractions: 1st 45-50°, 4.1 g, $n_D^{20}$ 1.5764; 2nd 135-170°, 0.8 g, crystallized; residue 18.0 g (tar).

The 1st fraction was mainly aniline, identified by preparing acetanilide. The 2nd fraction was recrystallized from ligroin to give 0.3 g of yellow plates with m. p. 184-185°, which sublimed on heating. They dissolved in ether and benzene. A mixture with 2-phenylindole, prepared by E. Fischer's method, melted at 184-186°; consequently, 2-phenylindole was isolated.

Another time 85.0 g of phenylhydrazone was decomposed in the presence of 0.9 g of cuprous chloride. Decomposition began at 215°, proceeded vigorously at a bath temperature of 250-260° and was accompanied by the evolution of ammonia and a gas, which passed through absorbers with water and sulfuric acid, burnt with a smoky flame and had the smell of benzene. We trapped 4.2 g of ammonia (for the anomalous reaction 3.4 g is required).

About 50 g of the mass obtained was placed in a flask, through which steam was passed. The mass became liquid. Approximately 1000 ml of distillate was collected, containing only traces of oil. Thus the reaction product did not contain substances, volatile in steam.

*Decomposition of p-chloroacetophenone phenylhydrazone.* 12.0 g of phenylhydrazone and 0.5 g of cuprous chloride were used. Decomposition began at 170° (bath temperature). At 240° we observed the vigorous evolution of ammonia and a combustible gas. 0.4 g of $NH_3$ was evolved (theoretical also 0.4 g) and 1.1 g of a turbid, colorless liquid distilled off in the range 68-115°. On distillation, we obtained 0.5 g of a substance with b. p. 170-185° (3 mm); a deposit of yellow crystals was formed on the walls of the apparatus; then decomposition began and distillation was stopped.

After recrystallization from an alcohol-water mixture, the yellow crystals (0.2 g) were converted into a finely crystalline, white powder with m. p. 195-196°. Literature data for 2-(4-chlorophenyl)-indole: m. p. 201-202° [3].

The thick black tar left in the reaction flask was treated with alcohol and partially dissolved. White curds (~ 1 g) were precipitated from the alcohol solution with water and these could not be converted into a crystalline state. They did not have a definite melting point and on heating, darkened and melted gradually.

Decomposition of phenylhydrazone of ethyl pyruvate. 6.0 g of hydrazone and 5.5 g of cuprous chloride were used in the reaction. Decomposition lasted about 2 hrs at a bath temperature of 210-250°. After cooling, the dark melt obtained was washed twice with 20 ml portions of hydrochloric acid (1:10) to remove catalyst. Then the solid mass was treated with ether (50 ml). After evaporating off the solvent, the ether extract gave a shiny, red, crystalline mass, which was distilled. At 150° (4 mm), we collected 1.50 g of a yellowish liquid, which quickly crystallized as fine plates. After two recrystallizations from alcohol, we isolated 1.05 g (19.1%) of a slightly yellowish, finely crystalline mass with m. p. 120.5-121.5°. A mixture with the starting hydrazone melted at 93-97°.

Found %: N 7.50, 7.65. $C_{11}H_{11}O_2N$. Calculated %: N 7.40. Literature data for 2-carboethoxyindole m. p. 107° [3].

Decomposition of pinacolin phenylhydrazone. 16.5 g of hydrazone and 0.3 g of cuprous chloride were heated in an Arbuzov flask. Evolution of ammonia began when the temperature of the bath reached 210°; then a yellowish liquid distilled off (69-85°). Then the bath temperature was raised to 250° and then a yellow liquid distilled over in the range 185-190°. We trapped 0.4 g of ammonia. In an attempt to distill the remaining reaction mixture in vacuum, we collected a small amount of a yellow liquid, boiling at 135-150° (13 mm), after which, a thick red liquid began to distill with decomposition. Aniline, detected as acetanilide, was found in the distillate, which came over at atmospheric pressure. The other products were not identified.

Decomposition of acetone methylphenylhydrazone. 16.0 g of hydrazone and 0.2 g of cuprous chloride were used in the reaction. The decomposition proceeded with the gentle evolution of gas at a bath temperature of 220-260°. We trapped 0.3 g of ammonia (for the anomalous reaction 0.84 g should be liberated). 11.5 g of a yellow liquid was distilled off from the reaction mixture in vacuum and 3.7 g of tar remained in the distillation flask. Distillation of the liquid at 15 mm gave the following fractions: 1st 85-88°, 2.7 g, $n_D^{21}$ 1.5512; 2nd 90-110°, 2.2 g, $n_D^{21}$ 1.5614; 3rd 111-118°, 5.1 g, $n_D^{21}$ 1.5568; residue 1.3 g.

The 3rd fraction was the starting hydrazone with $n_D^{21}$ 1.5578 and b. p. 116-117° (at 15 mm). The first fractions were not investigated more closely.

Decomposition of acetone phenylhydrazone under different conditions. a) 29.3 g of phenylhydrazone and 0.5 g of zinc chloride were heated in Arbuzov flask on a metal bath. The reaction began when the bath temperature reached 230° and proceeded for 3 hrs at a temperature of 240°-250°. The reaction was accompanied by the evolution of ammonia, which was absorbed in water and sulfuric acid and a gas, which passed through the absorbers and burnt with a smoky flame. 2.4 g of ammonia was liberated (theoretical 3.36 g). Distillation of the reaction mixture in vacuum gave 18.6 g of a yellow liquid.

On distilling this liquid, we collected the following fractions: 1st 40-50° (3 mm), 2.6 g, $n_D^{20}$ 1.5778; 2nd 98-102° (2 mm), 2.8 g; 3rd 103-105° (2 mm), 12.5 g, $n_D^{20}$ 1.6016; the residue was a small amount of a mobile cherry red tar.

The 1st fraction gave a crystalline product with acetic anhydride, which melted at 112.5-114° after boiling with animal charcoal and recrystallization from water, i. e., it was acetanilide (mixed melting point). Consequently, the main part of the first fraction was aniline.

The 2nd and 3rd fractions crystallized on standing and were recrystallized from aqueous alcohol to give 14.5 g (60%) of 2-methylindole with m. p. 58.5-59.5°.

On heating 2-methylindole with acetone phenylhydrazone in the presence of cuprous chloride, tar formation occurred and ammonia was evolved at 190°. The anomalous product was not isolated from the thick reaction mixture.

b) 57.1 g of phenylhydrazone and 1.0 g of cuprous chloride were heated under the same conditions as in the first experiment. The gas, passing through the ammonia trap, was passed through an acid solution of $KMnO_4$ and bromine water. We observed the decoloration of the bromine water without the evolution of HBr and the $KMnO_4$ solution (rapidly), if it was heated to 40°. The gas causing the decoloration, had a smell reminiscent of the smell of benzene and burnt quietly with a smoky flame on ignition. During the reaction, which lasted for 195 min, 2.5 g of a gas, which was not absorbed by acid, was liberated. We trapped 3.1 g of ammonia (theoretical 3.27 g). During the reaction, 14.5 g of a yellow liquid distilled off and then a further 25.1 g of reaction product was distilled off in vacuum (14 mm) to leave a residue of tar. Subsequent fractionation in vacuum gave the following fractions: 1st 42° (50 mm), a few drops of a colorless liquid; 2nd 79-83° (16 mm), $n_D^{20}$ 1.5630, 15.35 g; 3rd 140-146° (16 mm), $n_D^{20}$ 1.5818, 13.25 g; 4th 148-150° (16 mm) (decomp.); 5th – tar.

A second distillation of the 3rd and 4th fractions gave 13.1 g (40.7%) of 2-methylindole-1-aminide of acetone with b. p. 139-141° (12 mm), $n_D^{20}$ 1.5805. From the 2nd fraction we obtained acetanilide (m. p. 112.5-113°), i. e., it was mainly aniline.

c) 16.2 g of phenylhydrazone and 20.7 g of cuprous chloride were heated in a distillation apparatus on a metal bath. At 160° (in the bath) the liquid reaction mixture began to boil and frothed vigorously. The process gradually speeded up and ended with the reaction mixture coming out of the flask, when even cooling the flask with water did not help. The brown reaction mixture became green in air. If the reaction vessel was not cooled, then an explosion occurred in which a voluminous, yellow smoke was formed.

d) From a catalytic decomposition using 16.4 g of phenylhydrazone and 0.2 g of nickelous chloride, we obtained 7.1 g of a crystalline substance with m. p. 58-59°, corresponding to 2-methylindole with the characteristic smell of indole, and 0.95 g of aniline. The decomposition was accompanied by the evolution of ammonia and a gas, which passed through traps with water and sulfuric acid and burnt on ignition.

The reaction of phenylhydrazine with cuprous chloride and zinc chloride. On mixing different weights of phenylhydrazine and cuprous chloride, we observed heating up from 19 to 65°. After heating the mixture to 80°, vigorous evolution of heat began, at first without the formation of ammonia. The reaction finished with an explosion, when the temperature of the mixture reached 260°.

The reaction of phenylhydrazine with zinc chloride was studied similarly; in this case the mixture heated up to 80°. On heating the mixture, which crystallized on cooling, above 100°, decomposition began with the evolution of ammonia and benzene vapor.

## SUMMARY

1. We studied the catalytic decomposition of the phenylhydrazones of acetone, methyl isopropyl ketone, pinacolin, pyruvic acid, ethyl pyruvate, acetophenone and p-chloroacetophenone and the methylphenylhydrazone of acetone in the presence of cuprous chloride.

2. It was established that in catalytic decomposition in the presence of cuprous chloride, ketone phenylhydrazones, not containing $CH_2$ groups next to the carbonyl, do not, as a rule, form indoles, corresponding to the scheme of the Fischer reaction.

We isolated the anomalous reaction products of the phenylhydrazones of acetone and methyl isopropyl ketone and established their structure.

3. We found that sulfanilic acid is a catalyst of the anomalous Fischer reaction.

4. We showed the analogy between and gave the general scheme for the reaction mechanism of the catalytic decomposition of phenylhydrazine, the anomalous decomposition of some ketone phenylhydrazones and the formation of nitriles fromaldehyde phenylhydrazones, first found by A. E. Arbuzov in 1911-1913.

## LITERATURE CITED

[1] A. E. Arbuzov, J. Russ. Chem. Soc. 45, 74 (1913).

[2] A. E. Arbuzov and O. M. Shapshinskaya, Trans. Kazan Inst. Chem. Tech. 19-20, 27 (1955).

[3] Beilst. 4 Aufl. XX.

[4] K. Alder and H. Niklas, Lieb. Ann. 585, 97 (1954).

[5] P. Neber, Ber. 55, 826 (1922); Ch. A. 16, 3474 (1922).

[6] P. Neber and E. Keppler, Ber. 57, 778 (1924).

[7] A. Kliegel and A. Schmalenbach, Ber. 56, 1517 (1923).

[8] A. E. Arbuzov and V. M. Tikhvinsky, J. Russ. Chem. Soc. 45, 69 (1913); Ber. 43, 2301 (1910).

[9] R. J. F. Struthers, Chem. Zentr. 1905, I, 1232.

[10] K. Clusius and M. Hoch, Helv. Chim. Acta 33, 2122 (1950).

[11] G. Reddelien, Lieb. Ann. 388, 179 (1912).

[12] A. M. Buswell, J. R. Downing, and W. H. Rodebusch, J. Am. Chem. Soc. 62, 2759 (1940).

[13] P. F. Holt and B. P. Hughes, J. Chem. Soc. 1953, 1666.

[14] J. Beihringer and A. Busch, Ber. 36, 339 (1903).

[15] A. E. Arbuzov and Yu. P. Kitaev, J. Gen. Chem. 27, 2328 (1957).*

[16] H. Wieland, Ber. 45, 492 (1912).

[17] M. P. Grammaticakis, Bull. Soc. Chim. 14, 438 (1947).

[18] F. Just, Ber. 19, 1208 (1886).

[19] R. Walther, J. pr. Ch. (2) 53, 463 (1896).

[20] G. Oddo and E. Puxeddu, Ber. 38, 2752 (1905).

[21] G. J. Bloink and K. H. Pausacker, J. Chem. Soc. 1952, 661.

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# SOME DETAILS OF THE PREPARATION OF THE FREE RADICAL α,α-DIPHENYL-β-TRINITROPHENYLHYDRAZYL

A. E. Arbuzov and F. G. Valitova

In recent years certain free radicals have been used as standards for calibrating magnetic fields in experiments on electron magnetic resonance. Of the free radicals used for this purpose, a radical of the hydrazyl type – α,α-diphenyl-β-trinitrophenylhydrazyl – has been used the most. It is exceptionally stable and can be stored for years in an ordinary test tube without apparent change.

Goldschmidt and Renn [1] prepared the free radical α,α-diphenyl-β-trinitrophenylhydrazyl.

The method of preparing it was described in detail in the article published by them. However, though following the author's instructions, we could never prepare the hydrazyl radical in an at all satisfactory yield.

In finding out the reason for the poor yields of the hydrazyl, we established by a series of experiments that absolutely pure α,α-diphenylhydrazine must be used for successful synthesis and therefore great care must be taken in preparing the latter.

E. Fischer [2] was the first to prepare α,α-diphenylhydrazine by reducing diphenylnitrosamine with zinc dust in glacial acetic acid. The author did not mention the hydrazine yield. Certain modifications that we made to separate details of the Fischer synthesis have resulted in a reliable method of preparing chemically pure unsymmetrical diphenylhydrazine and then from it the free radical.

One of the main conditions for successful hydrazine synthesis was the use of finely pulverized zinc dust with no traces of oxidation (Kahlbaum type). In this case the hydrazine yield was on the average 35%.

After that, in accordance with [1], the diphenylhydrazine was treated with picryl chloride to give α,α-diphenyl-β-trinitrophenylhydrazine. The free radical, α,α-diphenyl-β-trinitrophenylhydrazyl, was readily prepared by oxidizing the latter with lead dioxide.

## EXPERIMENTAL

Preparation of α,α-diphenylhydrazine. To be successful, the experiment required a vigorous stirrer. Contrary to the directions of E. Fischer, in our experiments the zinc dust was not placed in the flask beforehand, but was added during the course of the reaction in small portions. On using 60 g of diphenylnitrosamine, 95 g of zinc dust and 250 g of glacial acetic acid, the reaction was complete in 4-5 hrs. The end of the reaction was determined by Fischer's method, i. e., when a filtered test sample did not give a green-blue color on adding strong hydrochloric acid.

After filtering off the precipitate of zinc acetate and excess zinc dust, approximately a quarter of the solvent was evaporated off under reduced pressure at a bath temperature no higher than 30-40°. If these conditions were not observed, the solution darkened and a tar was produced. The residue was diluted with an equal volume of water and then 1.5-1.75 liters of strong hydrochloric acid (d 1.19) added. After 1-2 hrs, grey-blue, needle-like crystals separated from the solution. The crystals were filtered off and dissolved in hot 10% hydrochloric acid (1.5-2 liters) and after adding animal charcoal, the solution was brought to boiling.

The solution obtained was filtered and to the filtrate was again added 1.5-2 liters of strong hydrochloric acid (d 1.19). On cooling, the solution deposited white crystals with a bluish tint of α,α-diphenylhydrazine hydrochloride, which were filtered off and washed slightly with water. Without further purification the substance was quite suitable for subsequent operations.

To isolate diphenylhydrazine itself, the crystals of diphenylhydrazine hydrochloride were treated with 30% aqueous sodium hydroxide solution (200-250 ml), and the bulk of the base floated to the surface in the form of dirty bluish curds. After half an hour, the alkaline solution together with the floating mass was extracted 3 times with ether (100 ml each), the ether solution washed with water till the disappearance of an alkaline reaction (to litmus), the ether distilled down to half its volume on a water bath and the rest of the ether removed in vacuum.

The residue – a dark red oil – was distilled in vacuum with an air condenser. The $\alpha,\alpha$-diphenylhydrazine distilled without signs of decomposition at 175° (10 mm) as a pale yellow oil, which quickly crystallized. In a series of experiments, a second distillation did not change the boiling point of the hydrazine.

The yield of pure $\alpha,\alpha$-diphenylhydrazine was 19.5 g (35%).

Then the preparation of the free radical $\alpha,\alpha$-diphenyl-$\beta$-trinitrophenylhydrazyl was carried out according to [1] and did not present any particular difficulties.

## SUMMARY

1. We thoroughly developed and improved the Fischer method for preparing pure $\alpha,\alpha$-diphenylhydrazine.

2. The $\alpha,\alpha$-diphenylhydrazine, prepared by the method described above may be used successfully for preparing the free radical $\alpha,\alpha$-diphenyl-$\beta$-trinitrophenylhydrazyl.

## LITERATURE CITED

[1] S. Goldsmidt and K. Renn, Ber. 55, 636 (1922).

[2] E. Fischer, Lieb. Ann. 190, 175 (1878).

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# THE REACTION OF HALOGEN DERIVATIVES OF SOME β-DISULFONES WITH SODIUM DIETHYLPHOSPHITE AND TRIETHYL PHOSPHITE

B. A. Arbuzov and N. P. Bogonostseva

The investigation we carried out previously [1] showed that the reaction of halogen derivatives of β-dicarbonyl compounds with sodium diethylphosphite and triethyl phosphite proceeds anomalously and results in the formation of reduction products of the halogen derivatives. Thus, for example, in the case of dibenzoylbromomethane, dibenzoylmethane is formed and tribenzoylmethane is formed from tribenzoylbromomethane.

We proposed a radical mechanism to explain the anomalous course of the reaction.

Later Kreutzkamp [2] also observed the reduction of chloro derivatives of β-dicarbonyl compounds by treating them with triethyl phosphite (chlorobenzoylacetone, tribenzoylchloromethane). He also put forward a hypothesis on the radical character of the conversions to explain the course of the reaction, as it is accelerated by ultraviolet radiation or peroxides.

Continuing our investigations, we studied the reaction of sodium diethylphosphite and triethylphosphite with the halogen derivatives of disulfones, which are known to be similar to the halogen derivatives of β-diketones.

We investigated the following halogen derivatives: $CBr_2(SO_2C_2H_5)_2$, $CCl_2(SO_2C_2H_5)_2$, $CH_3CBr(SO_2C_2H_5)_2$.

In this case, too, the reactions proceeded anomalously. Instead of the esters of the corresponding phosphinic acids, the corresponding disulfonylmethanes were obtained.

In the case of reactions of halogen derivatives of disulfones with triethylphosphite, besides reduction of the halogen derivatives, we observed also the alkylation of disulfonylmethanes.

Sodium diethylphosphite reacted with dibromodi-(ethylsulfonyl)-methane to give di-(ethylsulfonyl)-methane in 79% yield. In addition, we obtained a triethylphosphate and a high boiling product, which was found to be di-(diethylphosphonyl)-methane.

Due to the similarity of the physical properties and the analytical data of di-(diethylphosphonyl)-methane and tetraethylpyrophosphate, the formation of di-(diethylphosphonyl)-methane was proved by testing for insecticide effect. Tetraethylpyrophosphate has a strong insecticide effect, while di-(diethylphosphonyl)-methane does not. The reaction product of dibromodi-(ethylsulfonyl)-methane with sodium diethylphosphite was tested on grain weevils and showed no insecticide activity.*

The isolation of di-(diethylphosphonyl)-methane was somewhat unexpected. Its formation during the reaction may be explained by the reaction of sodium diethylphosphite with di-(ethylsulfonyl)-methane formed during the reaction

$$CH_2(SO_2C_2H_5)_2 + 2NaPO(OC_2H_5)_2 \rightarrow CH_2[PO(OC_2H_5)_2]_2 + 2C_2H_5SO_2Na$$

However, the experiments on the reaction of di-(ethylsulfonyl)-methane with sodium diethylphosphite did not give positive results.

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* We would like to thank M. A. Kudrina (Kazan Branch of the Academy of Sciences USSR) for testing the insecticide effect of the preparations.

The reaction between dichlorodi-(ethylsulfonyl)-methane and sodium diethylphosphite proceeded analogously with the formation of di-(ethylsulfonyl)-methane and triethylphosphate. We could not isolate di-(diethylphosphonyl)-methane in this case.

The reaction between sodium diethylphosphite and methyldi-(ethylphosphonyl)-methane bromide proceeded in a similar way. Methyldi-(ethylsulfonyl)-methane and triethylphosphate were obtained.

The reaction of halogen derivatives of disulfonylmethanes with triethylphosphite was more complicated and was accompanied by alkylation reactions. Thus, reaction of dichloro-(ethylsulfonyl)-methane with triethylphosphite gave di-(ethylsulfonyl)-methane and ethyldi-(ethylsulfonyl)-methane.

Ethyldi-(ethylsulfonyl)-methane was also prepared by reacting triethylphosphite with dibromodi-(ethylsulfonyl)-methane. Only the reduction product – methyldi-(ethylsulfonyl)-methane – was isolated in the case of methylbromodi-(ethylsulfonyl)-methane and triethylphosphite. In all cases, the reactions were accompanied by the formation of triethylphosphate. The alkylating reagent was, probably, triethylphosphite. However, direct experiments of alkylating di-(ethylsulfonyl)-methane with triethylphosphite did not give positive results.

The mechanism of the interesting reactions between halodisulfonylmethanes and sodium diethylphosphite or triethylphosphite cannot be considered as elucidated. Oxidation-reduction reactions take place. These reactions proceed when care is taken not to allow in moisture from the air. They also proceed when the air is replaced by nitrogen. Therefore, it is improbable that the oxidation-reduction processes occur due to the hydrogen and oxygen of water or aerobic oxygen.

It is known from the literature that halogen derivatives of disulfonylmethane are readily reduced. Thus, dibromodi-(butylsulfonyl)-methane was reduced to di-(butylsulfonyl)-methane with potassium iodide [3]. Di-(ethylsulfonyl)-diiodomethane was reduced to di-(ethylsulfonyl)-methane when treated with sodiomalonic ester [4]. The latter reaction is particularly close in character to the conversions described in this work.

It seems to us that, most probably, the reactions given in this report occur with the participation of free radicals.

## EXPERIMENTAL

Preparation of ethyl mercaptan. Of all the methods described for the preparation of ethyl mercaptan, the most rapid and effective is the method of preparing it from thiourea. As a basis we used the method of preparing n-dodecyl mercaptan [5], but the conditions were considerably changed and simplified. By this method it was possible to prepare considerable amounts of ethyl mercaptan without difficulty.

76 g of thiourea, 100 ml of rectified alcohol and 156 g of ethyl iodide, or 109 g of ethyl bromide were placed in a round-bottomed flask with a Wurtz head and a straight condenser, and while the flask was shaken, it was carefully heated on a water bath. It was necessary to take care that the alkyl halide and the alcohol did not distill off.

After solution of the thiourea, a solution of 50 g of sodium hydroxide in 150 ml of water was quickly added and the solution immediately heated on a water bath until the product distilled off. The ethyl mercaptan was collected in an ice-cooled receiver. To the outlet of the adapter was attached a rubber tube, which was immersed in a flask over concentrated potassium permanganate solution.

Strong cooling of the receiver and removal of the mercaptan vapor in the permanganate solution eliminated the smell and considerably increased the yield of product.

The ethyl mercaptan was washed free from alcohol with water and dried overnight with baked sodium sulfate; then it was distilled from an Arbuzov flask with ground glass joints.

From the given amounts of materials, we obtained 47.5 g (97.4%) of crude product or 45 g (92.2%) of dry ethyl mercaptan. The operation required 2.5-3 hours.

Reaction of sodium diethylphosphite with dibromodiethylsulfonylmethane. The reaction was carried out in a round-bottomed flask with a reflux condenser, containing an ether solution of sodium diethylphosphite (6 g of diethylphosphorus acid, 1 g of metallic sodium and 100 ml of absolute ether).

6.8 g of dibromodiethylsulfonylmethane [6], dissolved in dry benzene (dissolved by heating), was added dropwise to the sodium diethylphosphite. The reaction proceeded vigorously and the reaction mixture boiled up energetically. A voluminous white precipitate formed and the liquid became yellow. The precipitate was sodium bromide; the yield of it was quantitative.

After removal of the ether and the benzene from the filtrate, crystals deposited with m. p. 102-104°. They did not depress the melting point of diethylsulfonylmethane. The yield was 3 g.

The filtrate was distilled in vacuum; fractions were collected: 1st 60-73° at 2-2.5 mm, 3.17 g, $d_4^{20}$ 1.0668, $n_D^{20}$ 1.4073 (corresponding to triethylphosphate); 2nd 132-135° at 0.5 mm, 2.5 g, $d_{20}^{20}$ 1.1878, $n_D^{20}$ 1.4300 [corresponding to di-(diethylphosphonyl)-methane].

Analysis of 2nd fraction. Found %: C 35.69; H 7.46; P 20.9. $C_9H_{22}O_6P_2$. Calculated %: C 37.05; H 7.70; P 21.5.

Reaction of triethylphosphite with diethylsulfonylmethane dibromide. 30 g of triethylphosphite was added to 17 g of diethylsulfonylmethane dibromide without solvent. The reaction proceeded very vigorously and the temperature rose until the triethylphosphite boiled. At the end of the reaction, the mixture was heated on a water bath for 2 hrs.

After six distillations with a water and an oil pump from an Arbuzov flask or with a Widmer fractionating column, we isolated the following fractions: 1st 52-71° at 12 mm, 6.4 g, $n_D^{20}$ 1.4170, $d_{20}^{20}$ 0.9742 (triethylphosphite); 2nd 51-60° at 1 mm, 5.33 g, $n_D^{20}$ 1.4165, $d_{20}^{20}$ 1.0697; 3rd 68° at 1 mm, 3.7 g, $n_D^{20}$ 1.4130, $d_{20}^{20}$ 1.700 (triethylphosphate); 4th 151-152° at 2 mm, 6 g (crystallized).

The product in the 4th fraction was readily soluble in benzene, ether, alcohol, chloroform and carbon tetrachloride. After three recrystallizations from benzine and drying in a vacuum pistol, the product melted at 77-78° and formed white needles.

Found %: C 37.39, 37.15; H 7.04, 6.91; S 28.11, 28.4. M 229. $C_7H_{16}O_4S_2$. Calculated %: C 36.84; H 7.46; S 28.07. M 228.

Mixing with synthetic [7] propylidenediethylsulfone did not depress the melting point.

Reaction of methyldiethylsulfonylmethane bromide with sodium diethylphosphite. 4.6 g of methyldiethylsulfonylmethane bromide [8], dissolved in dry benzene, was poured into an ether solution of sodium diethylphosphite (2.5 g of diethylphosphorus acid, 0.41 g of sodium and 30 ml of dry ether). The reaction proceeded vigorously while the ether boiled vigorously and formed a voluminous precipitate on heating on a water bath for 2 hrs.

We isolated: 1.8 g of sodium bromide, a fraction with b. p. 83-115° at 7 mm, $d_{20}^{20}$ 1.0980, $n_D^{20}$ 1.4260, methyldi-(ethylphosphonyl)-methane (2 g) with m. p. 75-78° (identified by a mixed melting point with synthetic material and confirmed by the preparation of the bromide) and triethylphosphate with b. p. 86° at 9 mm, $d_{20}^{20}$ 1.0663, $n_D^{20}$ 1.4073 (0.45 g).

Reaction of methyldiethylsulfonylmethane bromide with triethylphosphite. 5 g of triethylphosphite (excess triethylphosphite was used as the solvent) was poured into 4 g of methyldiethylsulfonylmethane bromide. The reaction proceeded vigorously with the triethylphosphite boiling and the evolution of white vapor. It was cooled with water. At the end of the vigorous reaction, the reaction mixture was boiled for 2 hrs on a water bath, after which it appeared as a slightly yellowish liquid.

On distillation, we isolated the following fractions: 1st up to 50° at 6 mm, 0.7 g, $n_D^{20}$ 1.4142, $d_{20}^{20}$ 0.9711 (triethylphosphite); 2nd 70-90° at 5 mm, 1.25 g, $n_D^{20}$ 1.4170, $d_{20}^{20}$ 1.0612 (similar to triethylphosphate); 3rd 166-172° at 5 mm, 1.64 g; crystallized as white needles, which did not depress the melting point of methyldiethylsulfonylmethane. After separation of the crystals, the liquid part had b. p. 166-167° at 9 mm, $n_D^{20}$ 1.4500, $d_{20}^{20}$ 1.2060; weight 0.86 g (containing 12.5 and 12.98% phosphorus).

Reaction of sodium diethylphosphite with diethylsulfonylmethane dichloride. 4 g of diethylsulfonylmethane dichloride [7] was added to an ether solution of sodium diethylphosphite (4.5 g of diethylphosphorus acid, 0.72 g of sodium and 50 ml of dry ether). Heat was evolved. The reaction mixture was heated on a water bath for 4 hrs.

We isolated 2.95 g of sodium chloride and 1.65 g of a crystalline product with m. p. 102-104°, which was diethylphosphonylmethane (a mixed melting point was not depressed).

From the liquid part we isolated 3.7 g of triethyl phosphate with b. p. 84-86° at 7 mm, $n_D^{20}$ 1.4095, $d_{20}^{20}$ 1.0721 (containing 16.82 and 17.08% of phosphorus; calculated 17.04%).

Reaction of diethylsulfonylmethane dichloride with triethylphosphite in a nitrogen atmosphere. 3 g of triethylphosphite was poured into 15 g of diethylsulfonylmethane dichloride. Air was flushed out of the system with nitrogen. The reaction mixture heated up. It was heated on a boiling water bath under a steady stream of nitrogen for 2 hrs. No crystals were seen in the flask. On cooling the solution, 0.75 g of crystals with m. p. 100-102° were deposited. A mixture with diethylsulfonylmethane melted without depression.

On distilling the liquid part, we isolated the excess triethylphosphite and a fraction with b. p. 47-53° at 2 mm, $d_{20}^{20}$ 1.0544, $n_D^{20}$ 1.4205. The residue crystallized and the crystals melted at 73-75°, which was not depressed by mixing with ethyldiethylsulfonylmethane. The yield was 0.45 g.

## SUMMARY

1. The reactions of the halogen derivatives of β-disulfones studied with sodium diethylphosphite and triethylphosphite proceeded anomalously and the expected esters of phosphinic and diphosphinic acids were not obtained.

2. The reduction products of the starting disulfones and triethylphosphate were the main products.

The ethylation products of disulfones were also obtained in the reactions with triethylphosphite.

## LITERATURE CITED

[1] B. A. Arbuzov and N. P. Bogonostseva, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 837.*

[2] N. Kreutzkamp, Naturwiss. 42, 415 (1955).

[3] R. Stutz and R. Shriner, J. Am. Chem. Soc. 55, 1242 (1933).

[4] O. Bischoff, Ber. 36, 487 (1897).

[5] Org. Syntheses, N. Y. 21, 21 (1941).

[6] H. Böhme, Ber. 69, 1610 (1936); E. Baumann, Ber. 19, 2811 (1884).

[7] E. Fromm, Lieb. Ann. 253, 150, 158 (1889).

[8] R. Escales and E. Baumann, Ber. 19, 2815 (1884).

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* Original Russian pagination. See C.B. Translation.

# SYNTHESES OF SOME PHOSPHONE SULFIDES AND PHOSPHONE SULFONES

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Phosphone sulfones of the form $RSO_2CH_2PO(OR')_2$ are of considerable interest. Similar to β-keto- or β-carbalkoxysulfones [1], one might expect the formation of anions of the type $RSO_2{=}CHPO(OR)_2$ from them in an alkaline medium.

We tried to prepare esters of phosphinic and diphosphinic acids, containing sulfone groups, by treating halogen derivatives of β-disulfones with triethylphosphite or sodium diethylphosphite [2]. However, we did not get the expected esters. The reactions proceeded anomalously.

In this work we used the reaction of sodium mercaptides on the available ethyl chloromethylphosphinate to prepare β-phosphone sulfides [3].

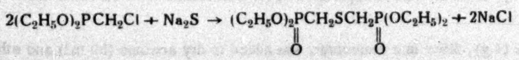
$$RSNa + ClCH_2PO(OC_2H_5)_2 \rightarrow RSCH_2PO(OC_2H_5)_2 + NaCl$$

Treatment with ethylmercaptide gave ethyl-(diethylphosphonyl)-methylsulfide in 85.6 % yield of crude product. Treatment with phenylmercaptide gave phenyl-(diethylphosphonyl)-methylsulfide.

Oxidation of ethyl-(diethylphosphonyl)-methylsulfide with acetyl peroxide gave the corresponding sulfone.

Oxidation of phenyl-(diethylphosphonyl)-methylsulfide with acetyl peroxide gave a crystalline product with m. p. 145-148°, for which we could not get satisfactory analytical data.

On reacting the ethyl chloromethylphosphinate with anhydrous sodium sulfide we obtained the corresponding sulfide



$$2(C_2H_5O)_2PCH_2Cl + Na_2S \rightarrow (C_2H_5O)_2\underset{\underset{O}{\|}}{P}CH_2SCH_2\underset{\underset{O}{\|}}{P}(OC_2H_5)_2 + 2NaCl$$

Oxidation of the sulfide, with acetyl peroxide gave the corresponding sulfone.

## EXPERIMENTAL

Preparation of ethyl-(diethylphosphonyl)-methylsulfide. Sodium mercaptide was prepared from 6 g of ethyl mercaptan in 50 ml of dry ether and 1.85 g of sodium. Ethyl chloromethylphosphinate [3] (15 g) was added to the mercaptide. The whole was heated on a water bath for 2 hrs. Then the ether was distilled off and heating continued on a boiling water bath for 2 hrs. After separating off the sodium chloride (4.7 g) and distilling through a Widmer column, we isolated the following fractions: 1st 4.7 g, 129-133° at 9 mm, $d_{20}^{20}$ 1.1093, $n_D^{20}$ 1.4610 and 2nd 6.0 g, 133-133.5° at 9 mm, $d_{20}^{20}$ 1.1033, $n_D^{20}$ 1.4630.

By successive distillations of these fractions, we isolated pure diethylphosphonyl sulfide:

b. p. 127-127.5° at 7 mm, $d_{20}^{20}$ 1.1052, $n_D^{20}$ 1.4650. Found %: S 15.13; P 14.27. $C_7H_{17}O_3SP$. Calculated %: S 15.1; P 14.15.

Preparation of ethyl-(diethylphosphonyl)-methylsulfone. Ethyl-(diethylphosphonyl)-methylsulfide with b. p. 127-127.5° at 7 mm (2 g) was oxidized with an ether solution of acetyl peroxide (10 ml of solution, containing 0.5 g of active oxygen), while cooled with snow. The oxidation proceeded vigorously; the peroxide was added dropwise so that the temperature did not rise above +2°. After 2 days the ether was distilled off. The acetic acid was removed in vacuum at 40-50 mm.

On distilling the residue, we obtained 1.9 g of a product with b. p. 213° at 28 mm. After a second distillation, we obtained a pure product:

b. p. 194° at 11.5 mm, $d_{20}^{20}$ 1.2271, $n_D^{20}$ 1.4560. Found %: S 13.44; P 12.14. $C_7H_{17}O_5SP$. Calculated %: S 13.11; P 12.7.

Preparation of phenyl-(diethylphosphonyl)-methylsulfide. From 11 g of phenyl mercaptan and 2.3 g of sodium in 100 ml of ether, a mercaptide was obtained by heating under reflux for 16 hrs. 20 g of ethyl chloromethylphosphinate was gradually added to the mercaptide. The reaction went vigorously. For completion of the reaction, the whole was heated to the boiling point of the ether for 3 hrs. The precipitate was separated off (10 g).

After evaporating off the ether and distilling the residue in vacuum, we obtained 5.7 g of a fraction with b. p. 177-179° at 7 mm, $d_{20}^{20}$ 1.1751, $n_D^{20}$ 1.5450. After a second distillation, we obtained 4 g of a substance:

b. p. 167-168° at 3 mm, $d_{20}^{20}$ 1.1736, $n_D^{20}$ 1.5483. Found %: S 12.18; P 11.78. $C_{11}H_{17}O_3PS$. Calculated %: S 12.31; P 11.92.

Oxidation of phenyl-(diethylphosphonyl)-methylsulfide. An ether solution of acetyl peroxide (16 ml, containing 0.71 g of active oxygen) was carefully added to 4 g of sulfide, cooled in snow. The following day, the ether and acetic acid were removed. The residue crystallized as a mass, saturated with tar. After removal of the tar on a porous plate, we obtained a crystalline product with m. p. 100-102°. After three recrystallizations from water (charcoal), we obtained white crystals as dense clusters of needles. After drying in a vacuum pistol, the m. p. was 145-148°.

Analysis of the product met with difficulties. Reproducible figures could not be obtained.

Found %: C 41.33, 41.49; H 3.58, 4.31; S 13.05, 12.86; P 12.17, 9.78. $C_{11}H_{17}O_4PS$. Calculated %: C 48.55; H 6.16; S 11.6; P 11.23. $C_{11}H_{17}O_5PS$. Calculated %: C 45.2; H 5.82; S 10.96; P 10.61.

Preparation of di-(diethylphosphonyl)-dimethylsulfide. Sodium sulfide was prepared and purified by Karyakin's method [4]. After a series of experiments, the best results were obtained under the following conditions.

Sodium sulfide (4 g), dried in a desiccator, was added to dry acetone (50 ml) and ethyl chloromethylphosphinate (19 g) was added to it. On adding the chloroester, a blue color appeared, which disappeared on shaking. The whole was heated on a water bath for 5 hrs. After separating off the sodium chloride by centrifuging (3.5 g was obtained) and removing the acetone, the residue was distilled. We obtained the following fractions: 1st, 12.2 g with b. p. 50-165° at 2 mm and 2nd, 3.2 g with b. p. 165-193° at 2 mm. On redistilling the 2nd fraction, we obtained 2 g of a slightly yellowish liquid:

b. p. 191-192° at 2.5 mm, $d_{20}^{20}$ 1.1947, $n_D^{20}$ 1.4675. Found %: C 36.04, 35.54; H 6.92, 6.90; S 9.74; P 18.44. $C_{10}H_{24}O_6P_2S$. Calculated %: C 35.92; H 7.19; S 9.59; P 18.59.

Preparation of di-(diethylphosphonyl)-dimethylsulfone. Di-(diethylphosphonyl)-dimethylsulfide (1.5 g), cooled in snow and salt, was oxidized with an ether solution of acetylperoxide. After removing the solvent and acetic acid, 1.2 g of needle-like crystals were deposited on long standing. After purification by recrystallization from petroleum ether, the sulfone had m. p. 76-78°.

Found %: C 32.69; H 6.31; S 8.74; P 17.11. $C_{10}H_{24}O_8P_2S$. Calculated %: C 32.79; H 6.55; S 8.74; P 16.93.

## SUMMARY

By treating ethyl chloromethylphosphinate with sodium mercaptide we synthesized ethyl-(diethylphosphonyl)-methylsulfide and phenyl-(diethylphosphonyl)-methylsulfide. By treating the ester of chloromethylphosphinic acid with sodium sulfide we prepared di-(diethylphosphonyl)-dimethylsulfide. Oxidation of the sulfides with acetyl peroxide gave the corresponding sulfones.

## LITERATURE CITED

[1] E. Fehnel and M. Carmack, J. Am. Chem. Soc. 71, 231 (1949).

[2] B. A. Arbuzov and N. P. Bogonostseva, J. Gen. Chem. 27, 2356 (1957).*

[3] M. I. Kabachnik and T. Ya. Medved, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, 638.

[4] Yu. V. Karyakin, Pure Chemical Reagents, Moscow-Leningrad, 1947, 385.**

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* Original Russian pagination. See C.B. Translation.

** In Russian.

# ADDITION OF ALCOHOLS TO ISOPRENE OXIDE

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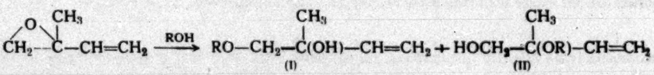
The addition of alcohols to the oxides of diene hydrocarbons has received very little study as yet; the data given in the literature deal only with divinyl oxide.

A. A. Petrov found that alcohols in the presence of alkali metal alcoholates add to divinyl oxide to give primary ethers (assumed to contain only small amounts of isomeric ethers as impurities), i.e., in accord with the Markovnikov rule, while in the presence of boron trifluoride etherate their addition is abnormal and secondary ethers are formed [1].

Kadesch [2] came to a similar conclusion when he studied the reaction of divinyl oxide with methyl alcohol. However, a more careful study of the latter reaction [3] revealed that a mixture of both isomeric ethers, with a predominance of the primary ether, is formed when the reaction is run in the presence of alcoholate. The products were not isolated in a pure form; they were identified as the 3,5-dinitrobenzoic acid derivatives.

It seemed of interest to us to study the addition of alcohols in the presence of various catalysts to the oxides of the divinyl homologs, piperylene and isoprene. The results of a partial study of the reactions with piperylene has been reported by one of us earlier (4).

We ran the reaction of isoprene oxide with methyl, ethyl, n-butyl and isobutyl alcohols in the presence of sodium alcoholate and in the presence of boron trifluoride etherate. In the presence of sodium alcoholate the main reaction products were the primary ethers. The tertiary ethers were isolated in much smaller amount.



$$\text{CH}_2\text{(O)C(CH}_3\text{)-CH=CH}_2 \xrightarrow{\text{ROH}} \underset{\text{(I)}}{\text{RO-CH}_2\text{-C(CH}_3\text{)(OH)-CH=CH}_2} + \underset{\text{(II)}}{\text{HOCH}_2\text{-C(CH}_3\text{)(OR)-CH=CH}_2}$$

The ratio of the different products is given in the table.

Reaction of Isoprene Oxide with Alcohols in the Presence of Sodium Alcoholate

| Alcohol | Amount of isomeric ethers in the mixture (in %) | | Total yield (in %) |
|---|---|---|---|
| | primary ether | tertiary ether | |
| Methyl | 89.1 | 10.9 | 36.7 |
| Ethyl | 91.0 | 9.0 | 46.6 |
| Isobutyl | 86.3 | 13.7 | 58.0 |
| n-Butyl | 90.8 | 9.2 | 72.3 |

The structure of the obtained products was decided on the basis of comparing their constants and rate of benzoylation. The tertiary ethers boil considerably higher than the primary ethers, and their benzoylation rate is several times faster.

All of the alcohols form tertiary ethers in the presence of boron trifluoride etherate. Besides the tertiary ethers, high-boiling fractions are formed in these reactions. Distillation of the fractions, obtained in the reactions with ethyl [5] and n-butyl alcohols, gave substances with a definite boiling point. They represent the products of the further addition of 2-alkoxy-2-methyl-3-butene to isoprene oxide. Analysis for hydroxyl group [5] and determination of the molecular weight confirm this conclusion.

The results obtained by us differ somewhat from those described earlier for unsym. disubstituted oxides.

A. A. Petrov and E. N. Pritula state [6] that the addition of alcohols to isobutylene oxide in the presence of sodium alcoholate leads to the formation of primary ethers. The latter, in their opinion, could be contaminated only with very small amounts of secondary ethers. A similar conclusion was reached by F. Ya. Perveev [7], who studied the addition of alcohols to 2-methyl-1,2-epoxy-5-hexen-3-yne, a disubstituted unsym. oxide of the vinylacetylene series. The observed difference in the results (addition in the presence of sodium alcoholates) can be explained either by the specific behavior of isoprene oxide when compared with other disubstituted unsym. oxides or, most probably, by the fact that due to the small amounts of oxides used by previous authors (0.1 mole [6]) in the reactions the tertiary ethers could be isolated. In a preliminary experiment, run with a small amount of isoprene oxide (0.18 mole) and ethyl alcohol in the presence of sodium ethylate, the tertiary ether was also not obtained by us in a pure form [5].

The peculiar behavior of allyl alcohol in its addition to the oxides of styrene and divinyl was mentioned in the paper by Swern and coworkers [8]. The addition of allyl alcohol to propylene oxide proceeds in a manner similar to other alcohols; in the case of styrene oxide in the presence of an alkaline catalyst the chief product is the secondary ether, while in the presence of sulfuric acid the primary ether is formed exclusively. In the case of divinyl oxide the secondary ether is formed predominantly with both catalysts. The authors explain such anomalous reaction behavior as being due to the specific influence of the phenyl group in styrene oxide on its polarization and of the vinyl group in allyl alcohol on the polarization of divinyl oxide.

In this connection we thought it of interest to study the addition of allyl alcohol to the disubstituted unsym. oxide – isoprene oxide. In this case, if the theories of Swern and coworkers are to be followed, even greater polarization of the oxide and progress of the reaction by the anomalous mechanism could be expected. When the reaction was run in the presence of alcoholate and in the presence of boron trifluoride etherate we failed to note any deviations from the usual course of the reaction, observed for saturated alcohols. In the presence of sodium ethylate we obtained a mixture of the primary and tertiary ethers with a predominant amount of the first, while with the boron trifluoride we obtained only the tertiary ether.

As a result, any specific influence exerted by allyl alcohol or its alcoholate, responsible, according to Swern and coworkers, for the anomalous polarization of an unsaturated oxide molecule in its reactions with alcohols, was not observed by us in the case of isoprene oxide.

## EXPERIMENTAL*

Isoprene α-oxide – 1,2-epoxy-2-methyl-3-butene – was obtained by the oxidation of isoprene with acetyl hydroperoxide (b.p. 79-80.5°, $n_D^{20}$ 1.4170, $d_4^{20}$ 0.8584).

### Addition of Methyl Alcohol to Isoprene Oxide

Expt. 1. To 185 ml of anhydrous methyl alcohol was added 0.15 ml of boron trifluoride etherate and gradually, with cold water cooling of the reaction flask, 34 g of isoprene oxide was added. The reaction mixture was heated on the water bath for 4 hours, and then the excess alcohol was distilled off. Vacuum-distillation of the residue through a Widmer column gave the following fractions:

1st, 13 g of 2-methoxy-2-methyl-3-buten-1-ol (II, R = $CH_3$).

B.p. 75-76° (50 mm), $n_D^{20}$ 1.4390, $d_4^{20}$ 0.9457, MR 32.47; Calc. 32.60.

Found %: C 62.58; H 10.40; OH 14.93. $C_6H_{12}O_2$ Calculated %: C 62.06; H 10.34; OH 14.65.

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* I. Aladzheva participated in the experimental portion of this study.

2nd, 4.5 g with b.p. 96 – 170° (10 mm), from which individual products could not be isolated on redistillation.

For benzoylation a mixture of 1.2212 g of oxide (I), 1.4113 g of benzoyl chloride and 1.1647 g of dimethylaniline was heated in a thermostat at 50° for 1 hour. Then 30 ml of water and 20 ml of carbon tetrachloride was added. Titration was with 0.5 N NaOH solution. The extent of benzoylation was 36.18%.

Expt. 2. A solution of 1 g of sodium in 200 ml of anhydrous methyl alcohol was treated with 34 g of isoprene oxide. The reaction mixture was heated on the water bath for 10 hours. The excess alcohol was distilled, and then further distillation was in vacuo using a Widmer column. The yield of 1-methoxy-2-methyl-3-buten-2-ol (I, R = $CH_3$) was 15.6 g.

B.p. 62.5-63° (50 mm), $n_D^{20}$ 1.4285, $d_4^{20}$ 0.9193, $MR_D$ 32.50; Calc. 32.60.

Found %: C 61.80; H 10.30; OH 15.56. $C_6H_{12}O_2$ Calc. %: C 62.06; H 10.34; OH 14.65.

The residue from the distillation was dissolved in 20 ml of anhydrous ether, and the residue was filtered. Distillation gave 1.7 g of 2-methoxy-2-methyl-3-buten-1-ol (II, R = $OCH_3$) with b.p. 75-79° (50 mm), $n_D^{20}$ 1.4385. The benzoylation went to the extent of 13.4% (run in the same manner as in the preceding experiment).

## Addition of Ethyl Alcohol to Isoprene Oxide

Expt. 1. The reaction was run with 170 ml of anhydrous ethyl alcohol, 0.15 ml of $BF_3$ etherate and 34 g of isoprene oxide by the method described in the preceding experiment. We obtained 24.8 g of 2-ethoxy-2-methyl-3-buten-1-ol (II, R = $C_2H_5$).

B.p. 52.3-53.3° (7 mm), $n_D^{20}$ 1.4380, $d_4^{20}$ 0.9227 and 6.1 g of a fraction with b.p. 90-120° (9 mm), which was not investigated closer.

Expt. 2. A solution of sodium ethylate, prepared from 160 g of ethyl alcohol and 1 g of sodium, was treated with 34 g of isoprene oxide. We obtained 22.3 g of 1-ethoxy-2-methyl-3-buten-2-ol (I, R = $C_2H_5$) with b.p. 45-46° (12 mm), $n_D^{20}$ 1.4720, $d_4^{20}$ 0.8971 and 2 g of 2-ethoxy-2-methyl-3-buten-1-ol (II, R = $OC_2H_5$) with b.p. 59-59.5° (12 mm), $n_D^{20}$ 1.4365, $d_4^{20}$ 0.9222.

## Addition of n-Butyl Alcohol to Isoprene Oxide

Expt. 1. The reaction was run with 150 ml of anhydrous n-butyl alcohol, 0.15 ml of $BF_3$ etherate and 34 g of isoprene oxide. The following fractions were obtained:

1st, 30.6 g of 2-butoxy-2-methyl-3-buten-1-ol (II, R = $C_4H_9$).

B.p. 80-81° (10 mm), $n_D^{20}$ 1.4390, $d_4^{20}$ 0.9030, $MR_D$ 46.04; Calc. 46.46.
Found %: C 68.19; H 11.45. $C_9H_{18}O_2$ Calc. %: C 68.35; H 11.39.

2nd, 11.6 g with b.p. 114-165° (10 mm).

The benzoylation, run under the conditions described in the preceding experiments, went to the extent of 50.7%.

Redistillation of the high-boiling fraction gave the reaction product of isoprene oxide and 2-butoxy-2-methyl-3-buten-1-ol.

B. p. 124-125° (17 mm), $n_D^{20}$ 1.4550, $d_4^{20}$ 0.9360, $MR_D$ 70.49.
$C_{14}H_{26}O_3$ Calc. 70.73.

Expt. 2. The reaction was run with a solution of sodium n-butylate, prepared from 160 ml of anhydrous n-butyl alcohol with 1 g of sodium, and 34 g of isoprene oxide. Distillation gave 42 g of 1-butoxy-2-methyl-3-buten-2-ol (I, R = $C_4H_9$).

B.p. 69.5-70.5° (10 mm), $n_D^{20}$ 1.4303, $d_4^{20}$ 0.8777, $MR_D$ 46.51. Calc. 46.46.
Found %: C 68.31; H 11.12; OH 10.9. $C_9H_{18}O_2$ Calculated %: C 68.35; H 11.39; OH 10.76.

Benzoylation went to the extent of 10.9%.

The working up and distillation of the residue gave 4.3 g of 2-butoxy-2-methyl-3-buten-1-ol (II, R = $C_4H_9$) with b.p. 80-81.5° (9 mm) $n_D^{20}$ 1.4380, $d_4^{20}$ 0.9037.

### Addition of Isobutyl Alcohol to Isoprene Oxide

Expt. 1. For reaction we took 170 ml of anhydrous isobutyl alcohol, 0.15 ml of $BF_3$ etherate and 34 g of isoprene oxide. The following fractions were obtained:

1st, 26.6 g of 2-isobutoxy-2-methyl-3-buten-1-ol (II, R = iso-$C_4H_9$). Benzoylation went to the extent of 64%.

B.p. 67-68° (8 mm), $n_D^{20}$ 1.4380, $d_4^{20}$ 0.9001, $MR_D$ 46.10; Calc. 46.46.
Found %: C 68.44; H 11.22; OH 10.80.
$C_9H_{18}O_2$ Calculated %: C 68.35; H 11.39; OH 10.76.

2nd, 12 g with b.p. 100-120° (8 mm).

Redistillation of the high-boiling fraction gave a number of fractions, not investigated closer.

Expt. 2. The experiment was run with a solution of sodium isobutylate, prepared from 175 ml of isobutyl alcohol with 1 g of sodium, and 34 g of isoprene oxide. The following fractions were obtained:

1st, 32 g of 1-isobutoxy-2-methyl-3-buten-2-ol (I, R = iso-$C_4H_9$):

B.p. 58.5-59° (8 mm), $n_D^{20}$ 1.4270, $d_4^{20}$ 0.8730, $MR_D$ 46.46; Calc. 46.46.
Found %: C 68.19; H 11.20; OH 10.91.
$C_9H_{18}O_2$ Calc. %: C 68.35; H 11.39; OH 10.76.

The benzoylation went to the extent of 11.4%.

2nd, 5.1 g of 2-isobutoxy-2-methyl-3-buten-1-ol (II, R = iso-$C_4H_9$), b.p. 67.5-70° (8 mm), $n_D^{20}$ 1.4362, $d_4^{20}$ 0.9012.

### Addition of Allyl Alcohol to Isoprene Oxide

Expt. 1. For reaction we took 180 ml of anhydrous allyl alcohol, 0.15 ml of $BF_3$ etherate and 40 g of isoprene oxide. The following fractions were obtained:

1st, 19 g of 2-allyloxy-2-methyl-3-buten-1-ol (II, R = $OC_3H_5$):

B.p. 77-78° (20 mm), $n_D^{20}$ 1.4530, $d_4^{20}$ 0.9392, $MR_D$ 40.89; Calc. 41.38.
Found %: C 67.67; H 9.62. $C_8H_{14}O_2$ Calc. %: C 67.60; H 9.86.

2nd, 13 g with b.p. 113-160° (13 mm).

Redistillation of this fraction gave a number of fractions, not investigated closer.

Expt. 2. The reaction was run with 170 ml of anhydrous allyl alcohol, 0.9 g of sodium and 30.5 g of isoprene oxide. The following fractions were obtained:

1st, 35 g of 1-allyloxy-2-methyl-3-buten-2-ol (I, R = $C_3H_5$).

B.p. 68.5-69.5° (22 mm), $n_D^{20}$ 1.4455, $d_4^{20}$ 0.9164, $MR_D$ 41.24; Calc. 41.38.
Found %: C 67.81; H 9.72. $C_8H_{14}O_2$ Calc. %: C 67.60; H 9.86.

2nd, 2.9 g of 2-allyloxy-2-methyl-3-buten-1-ol (II, R = $C_3H_5$) with b.p. 78-79° (21 mm), $n_D^{20}$ 1.4529, $d_4^{20}$ 0.9385.

## SUMMARY

1. The addition of methyl, ethyl, isobutyl, n-butyl and allyl alcohols to isoprene oxide was studied.

2. The addition of the above indicated alcohols to isoprene oxide in the presence of sodium alcoholate yields a mixture of isomeric ethers. The mixtures contain 86-91% of the primary ether and 9-14% of the tertiary ether.

3. In the presence of boron trifluoride etherate the alcohols add to isoprene oxide with the formation of tertiary ethers.

## LITERATURE CITED

[1] A. A. Petrov, J. Gen. Chem., 16, 1625 (1946).

[2] R. Kadesch, J. Am. Chem. Soc., 68, 41 (1946).

[3] P. Bartlett and S. Ross, J. Am. Chem. Soc., 70, 926 (1948).

[4] A. N. Pudovik and B. E. Ivanov, J. Gen. Chem., 26, 2771 (1956).*

[5] A. N. Pudovik and B. E. Ivanov, Trans. Kazan Univ., 116, Vol. 1, 141 (1956).

[6] A. A. Petrov and E. N. Pritula, J. Appl. Chem. (USSR), 28, 556, (1955).*

[7] F. Ya. Perveev, Bull. Leningrad State Univ., 2, 174 (1955).

[8] D. Swern, G. Billen, H. Knight, J. Am. Chem. Soc., 71, 1152 (1949).

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* Original Russian pagination. See C. B. Translation.

# SUBSTITUTION REACTIONS OF PHOSPHONIUM ACETATE AND PHOSPHONIUM ACETONE

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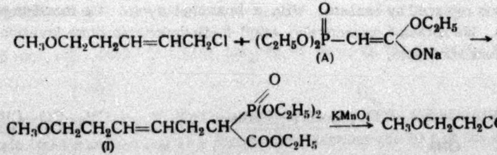
The chemical properties of phosphonium acetate and phosphonium acetone, forming the phosphorus analogs of malonates and acetoacetates, have been studied quite inadequately up to the present time. A. E. Arbuzov and co-workers who, in 1914, produced phosphonium acetate, in further work showed that, by the action on its metal derivatives of alkyl halides, the homologs of phosphonium acetate are formed [1, 2]. In this way they synthesized methyl- and benzylphosphonium acetates; and subsequently other homologs also were obtained [3, 4]. One of us and N. M. Lebedeva from reactions, for example, with $\alpha,\beta$-unsaturated ketones, nitriles, and carboxylic acid esters, showed that phosphonium acetate, phosphonium acetonitrile and their homologs could enter into addition reactions through the double bond [3, 5]. Phosphonium acetate, though with great difficulty, can be condensed with benzaldehyde and p-toluylaldehyde with formation of indene derivatives [6].

For phosphonium acetone, obtained in 1946 by A. I. Razumov and N. Petrov [7], at the present time a limited number of reactions are known – alkylation [8, 9] (with methyl and ethyl iodides), and addition reactions with unsaturated compounds [8]. Just recently reactions have been described of metal derivatives of phosphonium acetate and phosphonium acetone with acetyl chloride and chlorocarbonic ester [10].

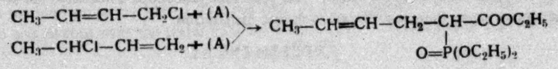
In the present work we have studied the reactions of metal derivatives of phosphonium acetate and phosphonium acetone with halogen allyl compounds, esters of $\alpha$-halogen-substituted carboxylic acids, bromoacetone and chloromethylbutyl ether. By action on the sodium derivative of phosphonium acetate (A) of 1-methoxy-5-chloropentene-3 the triethyl-(5-methoxypentenyl-2) phosphonium acetate (I) was obtained. By oxidation of (I) with potassium permanganate, methoxypropionic acid was separated and identified, thus indicating the correctness of the structure assigned to it.



$$CH_3OCH_2CH_2CH{=}CHCH_2Cl + \underset{(A)}{(C_2H_5O)_2\overset{O}{\overset{\|}{P}}}-CH{=}C\begin{matrix}OC_2H_5\\ONa\end{matrix} \longrightarrow$$

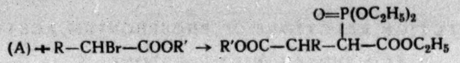
$$\longrightarrow \underset{(I)}{CH_3OCH_2CH_2CH{=}CHCH_2CH}\begin{matrix}\overset{O}{\overset{/\!/}{P}}(OC_2H_5)_2\\COOC_2H_5\end{matrix} \xrightarrow{KMnO_4} CH_3OCH_2CH_2COOH$$

In similar experiments with isomeric hydrochlorides of butadiene the same product was obtained, namely, triethyl-2-butenyl-phosphonium acetate. The reaction with the primary chloride proceeds normally; with the secondary it proceeds with complete allyl regrouping:



$$\begin{matrix}CH_3-CH{=}CH-CH_2Cl + (A)\\CH_3-CHCl-CH{=}CH_2 + (A)\end{matrix} \rightarrow CH_3-CH{=}CH-CH_2-\underset{O=P(OC_2H_5)_2}{\underset{|}{CH}}-COOC_2H_5$$

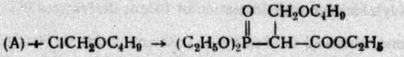
Moreover, we have also studied reactions of the sodium derivative of phosphonium acetate with esters of several α-chloro- and α-bromo-substituted carboxylic acids: with chloro- and bromoacetates, methyl-α-bromopropionate and ethyl-α-bromoisobutyrate. The reactions with chloroacetate proceed very slowly in ether and even in benzene solution; with bromoacetate easily and quickly in ether solution. The diethyl ester of diethylphosphonium-succinic acid was obtained. And similarly, the methylethyl ester of diethylphosphonium-methylsuccinic acid was synthesized.



$$(A) + R{-}CHBr{-}COOR' \rightarrow R'OOC{-}CHR{-}\overset{O=P(OC_2H_5)_2}{\overset{|}{C}H}{-}COOC_2H_5$$

Product yields were about 35%. Reaction of α-bromoisobutyrate with the sodium derivative of phosphonium acetate proceeds very slowly both in ether and benzene solutions. With prolonged heating of the reaction mixture sodium bromide is precipitated in small amount. In view of the small quantity of high-boiling fractions forming from the reaction the product did not separate in a pure state. It is evident that steric hindrance plays an important part in the progress of this reaction.

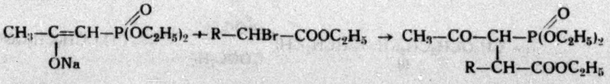
Thus, besides, the method of synthesizing phosphonium succinates and their homologs, including the addition of phosphonium acetate and its homologs to maleates and fumarates and their homologs, previously developed by us, the substitution reactions may also be used for synthesizing this type of compound. In carrying out reactions of sodium-phosphonium acetate with the chloromethylbutyl ester, the ethyl ester of α-diethylphosphonium-β-butoxypropionic acid was obtained:



$$(A) + ClCH_2OC_4H_9 \rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}\overset{CH_2OC_4H_9}{\overset{|}{C}H}{-}COOC_2H_5$$

The reaction with bromoacetone proceeds vigorously, but the reaction products resinify during distillation.

For synthesizing the homologs of phosphonium acetone the method of alkylating its sodium or potassium derivative with alkyl halides was the most convenient. By this method we had previously obtained methyl- and ethylphosphonium acetone [8]. Apparently the simpler and more convenient method of their synthesis, by the action on the bromoacetone homologs of phosphoric esters, does not lead to positive results, since the reactions in this case are mainly anomalous, with formation of unsaturated phosphoric esters [9, 11, 12]. We carried out reactions of the sodium derivative of phosphonium acetone with the ethyl esters of bromoacetic, α-bromopropionic, and α-bromoisobutyric acids, and with bromoacetone. The reaction with ethylbromoacetate proceeds easily in ether solution; with methyl-α-bromopropionate in ether it proceeds very slowly, and therefore the ether solution was replaced by benzene. With α-bromoisobutyrate the reaction proceeds very slowly, even in benzene solution. We obtained respectively: ethyl-β-diethylphosphonium levulinate and methyl-α-methyl-β-diethylphosphonium levulinate.



$$CH_3{-}\underset{ONa}{\underset{|}{C}}{=}CH{-}\overset{O}{\overset{/\!/}{P}}(OC_2H_5)_2 + R{-}CHBr{-}COOC_2H_5 \rightarrow CH_3{-}CO{-}\underset{R-CH-COOC_2H_5}{\underset{|}{CH}}{-}\overset{O}{\overset{/\!/}{P}}(OC_2H_5)_2$$

In the reactions with α-bromoisobutyrate a very small amount of high-boiling fractions was obtained; the reaction product was not separated in a pure state. In carrying out the reactions of sodium-phosphonium acetone with bromoacetone, diethylphosphonium, acetylacetone was obtained. Product yields in reactions with sodium-phosphonium acetone were about 30%. Reactions were carried out of sodium-phosphonium acetone with chloromethylethyl and chloromethylbutyl esters. The reactions proceeded smoothly, but it was not possible to separate the products owing to their resinification during distillation.

## EXPERIMENTAL

Action of sodium-phosphonium acetate on 1-methoxy-5-chloropentene-3. 35 g phosphonium acetate was gradually added to 150 ml of the dry ester and 3.4 g sodium mixed in a flask provided with mechanical stirrer, drop funnel and reflux condenser. After all the sodium had dissolved, 20 g 1-methoxy-5-chloropentene-3 was added to an ether solution. During heating of the reaction mixture a precipitate of sodium chloride settled as a thick greasy mass. After separating the precipitate and distilling off the ether the residue was distilled in vacuum. After several distillations 12 g of triethyl-(5-methoxypentenyl-2)-phosphonium acetate was obtained.

B. p. 167-169° at 4 mm, $n_D^{20}$ 1.4526, $d_4^{20}$ 1.0718, $MR_D$ 81.08; calc. 80.55. Found %: P 9.47. $C_{14}H_{27}O_6P$. Calculated %: P 9.62.

In small amount a fraction of b. p. 86-166° (4 mm) was also obtained, from which it was not possible to separate products of definite b. p.

8 g triethyl-(5-methoxypentenyl-2)-phosphonium acetate dissolved in 300 ml water was oxidized with potassium permanganate (10.5 g). After treating the reaction mixture 1.7 g of methoxypropionic acid was obtained of b. p. 105-106° at 9 mm, $n_D^{20}$ 1.4180.

Action of 1-chlorobutene-2 on sodium-phosphonium acetate. 21.4 g of the butene was added to an ether solution of the acetate prepared from 2.3 g of sodium, 150 ml ether, and 35 g phosphonium acetate. After treatment of the reaction mixture 13.5 g of triethyl-2-butenylphosphonium acetate was obtained.

B.p. 156-157° (10 mm), $n_D^{20}$ 1.4458, $d_4^{20}$ 1.0617, $MR_D$ 69.78; calc. 69.67. Found %: P 11.11. $C_{12}H_{23}O_5P$. Calculated %: P 11.15.

Action of 2-chlorobutene-3 on sodium-phosphonium acetate. The reaction was performed with the same amounts of reagents as in the preceding, but ether during the course of the experiment was replaced by benzene. The reaction was slow. As a result of the working and threefold distillation of the reaction mixture 10.8 g separated of triethyl-2-butenylphosphonium acetate of b. p. 154-155° (9 mm), $n_D^{20}$ 1.4430, $d_4^{20}$ 1.0661.

Synthesis of the diethyl ester of diethylphosphonium-succinic acid. 15 g of ethylbromoacetate was added to an ether solution of sodium-phosphonium acetate (1.54 g sodium and 15 g phosphonium acetate). The reaction mixture was heated for 6 hrs. Sodium bromide was filtered off, the ether distilled off, and the precipitate redistilled in vacuum. As a result of double distillation 6.0 g of the diethyl ester of diethylphosphonium succinic acid was obtained.

B. p. 165-166° at 3.5 mm, $n_D^{20}$ 1.4402, $d_4^{20}$ 1.1355, $MR_D$ 71.97; calc. 71.79. Found %: P 10.15. $C_{12}H_{23}O_7P$. Calculated %: P 10.00. Literature data [13]: b. p. 161-162° at 2 mm, $n_D^{20}$ 1.4410, $d_4^{20}$ 1.1333.

Methylethyl ester of methyl-(diethylphosphonium)-succinic acid. 11.2 g methyl-α-bromopropionate was added to an ether solution of sodium-phosphonium acetate (1.54 g sodium, 15 g phosphonium acetate). 8.6 g was obtained of the methylethyl ester.

B. p. 151-153° at 2.5 mm, $n_D^{20}$ 1.4432, $d_4^{20}$ 1.1434, $MR_D$ 71.94; calc. 71.79. Found %: P 10.32. $C_{12}H_{23}O_7P$. Calculated %: P 10.00.

Action of chloromethylbutyl ester on sodium-phosphonium acetate. The reaction was performed with sodium-phosphonium acetate (1.54 g sodium and 15 g phosphonium acetate) and 10 g of the chloromethylbutyl ester. 3.3 g was obtained of ethyl-α-diethylphosphonium-β-butoxypropionate.

B. p. 177-178° at 3 mm, $n_D^{20}$ 1.4415, $d_4^{20}$ 1.0612, $MR_D$ 77.23; calc. 76.40. Found %: P 9.55. $C_{13}H_{27}O_6P$. Calculated %: P 10.00.

Reactions with sodium-phosphonium acetone. 1) 20 g bromoacetate was added to an ether solution of sodium-phosphonium acetone prepared from 1.77 g sodium, 15 g phosphonium acetone, and 100 ml dry ether. The reaction mixture was heated over the water bath for 8 hrs. 6.5 g was obtained of ethyl-β-diethylphosphonium levulinate.

B. p. 148-149° at 3 mm, $n_D^{20}$ 1.4430, $d_4^{20}$ 1.1283, $MR_D$ 65.86; calc. 65.53. Found %: P 11.05. $C_{11}H_{21}O_6P$. Calculated %: P 11.07.

2) An ether solution of sodium-phosphonium acetone was prepared as before. To this was added 20 g methyl-α-bromopropionate. Heated for 12 hrs. There was little separation of sodium bromide. Ether was replaced by benzene, after which heating was continued for a further 4 hrs over the boiling water bath. 5.5 g was obtained of methyl-α-methyl-β-diethylphosphonium levulinate. The surface of the product was covered with a thin film that caused turbidity when shaken up.

B. p. 151-153° at 3 mm, $n_D^{20}$ 1.4556. Found %: P 11.04. $C_{11}H_{21}O_6P$. Calculated %: P 11.07.

3) We used 1.63 g sodium, 14 g phosphonium acetone, and 12 g bromoacetone. The reaction proceeded by the usual method in ether solution. 4.5 g was obtained of diethylphosphoniumacetonyl acetone.

B. p. 125-126° at 9 mm, $n_D^{20}$ 1.4510, $d_4^{20}$ 1.1415, $MR_D$ 58.99; calc. 59.27. Found %: P 12.80, 12.85. $C_{10}H_{19}O_5P$. Calculated %: P 12.40.

## SUMMARY

1. The reactions were studied of sodium-phosphonium acetate with isomeric chlorobutenes. The primary chlorobutene reacts normally, the secondary with allyl regrouping.

2. As a result of the reactions of sodium-phosphonium acetate with bromoacetate and α-bromopropionate, diethylphosphonium succinate and methylsuccinate were obtained; and with sodium-phosphonium acetone, respectively, diethylphosphonium levulinate and -methyllevulinate. Reactions with α-bromoisobutyrate proceed very slowly, evidently due to steric hindrance. It was not possible to separate the reaction products.

3. The reactions were studied of the sodium derivatives of phosphonium acetate and phosphonium acetone with bromoacetone and chloromethylbutyl ester.

## LITERATURE CITED

[1] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc. 46, 295 (1914).

[2] A. E. Arbuzov and A. I. Razumov, J. Russ. Chem. Soc. 61, 623 (1929).

[3] A. N. Pudovik and N. M. Lebedeva, J. Gen. Chem. 22, 2128 (1952).*

[4] G. M. Kosolapoff, Organophosphorus Compounds, New York, 1950.

[5] A. N. Pudovik and N. M. Lebedeva, J. Gen. Chem. 25, 2235 (1955).*

[6] A. N. Pudovik and N. M. Lebedeva, Proc. Acad. Sci. USSR 90, 799 (1953).

[7] A. I. Razumov and N. Petrov, Trans. Kazan Chem.-Tech. Inst. No. 10, 35 (1946).

[8] A. N. Pudovik and N. M. Lebedeva, J. Gen. Chem. 25, 1920 (1955).*

[9] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR 106, 263 (1956).*

[10] N. Kreutzkamp, Chem. Ber. 88, 195 (1955).

[11] A. N. Pudovik, J. Gen. Chem. 25, 2173 (1955);* Proc. Acad. Sci. USSR 105, 735 (1955).

[12] A. N. Pudovik and L. G. Biktimirova, J. Gen. Chem. 27, 1708 (1957).*

[13] A. N. Pudovik, Bull. Acad. Sci. USSR, Div. Chem. Sci. 926 (1952).*

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* Original Russian pagination. See C.B. Translation.

# ADDITION OF COMPLETE ESTERS OF PHOSPHORIC AND PHOSPHINIC ACIDS TO CONJUGATED SYSTEMS

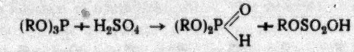
## I. ADDITION OF TRIALKYLPHOSPHITES TO ACRYLIC AND METHACRYLIC ACIDS

Gil'm Kamai and V. A. Kukhtin

The most important and the most studied method of synthesizing phosphinic esters is the reaction of trialkylphosphites with alkyl halides discovered by A. E. Arbuzov [1]. This reaction, known now as the "Arbuzov rearrangement," has been the subject of much research. With its aid a large number of different compounds have been obtained [2].

However, up to the present students of the Arbuzov rearrangement were limited to the study only of different halogen reagents; although it was possible to suppose that also other electronophil reagents not containing a halide, were capable of this reaction.

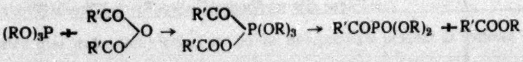
As has been shown by A. E. Arbuzov and P. I. Alimov [3], several inorganic acids react with trialkylphosphites, similar to the hydrogen chloride, as per scheme:



$$(RO)_3P + H_2SO_4 \rightarrow (RO)_2P\begin{matrix}\nearrow O\\ \searrow H\end{matrix} + ROSO_2OH$$

V. S. Abramov [4] found that trialkylphosphites are capable of combining with the carbonyl group, and are thus reformed into compounds of pentavalent phosphorus.

It was further established by the present authors [5] that organic acid anhydrides react with trialkylphosphites in the manner of the Arbuzov rearrangement:



$$(RO)_3P + \begin{matrix}R'CO\\ R'CO\end{matrix}\!\!>\!O \rightarrow \begin{matrix}R'CO\\ R'COO\end{matrix}\!\!>\!P(OR)_3 \rightarrow R'COPO(OR)_2 + R'COOR$$

By prolonged study of the action of different electronophil reagents with trialkylphosphites we found that unsaturated acids react fairly actively with complete phosphoric acid esters. Especially active is the reaction of acrylic acid with trialkylphosphites. With slow addition of acrylic acid to the phosphite, within 10-15 min after start of the reaction, temperature began to rise quickly, and reached 135° in the case of triethylphosphite. In mixing trialkylphosphites with methacrylic acid only a small rise in temperature is noted (5-10°). But in heating up to 70-100° temperature begins to rise quickly, reaching 130-150°, and remaining for some time at this level after heating has stopped. In such case the smell of phosphite and acid disappears fairly quickly, and a test with a copper monohalide indicates the absence of trivalent phosphorus in the reaction mixture.

Methacrylic acid reacts with triethylphosphite and without heating if the mixture of reagents is left to stand for some days at room temperature.

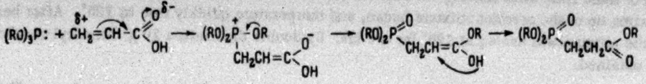
We were able to separate the products of the union of trialkylphosphites with acrylic and methacrylic acids, with yields up to 60%. Study of the products obtained showed that they do not contain the double bond and the acid group, and are complete esters of the corresponding phosphono-carboxylic acids.

| No. | Formula | B. p. (pressure in mm) | $n_D^{20}$ | $d_0^{20}$ | $MR_D$ |  | % Phosphorus |  | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | found | calculated | found | calcu-lated |  |
| 1 | $(CH_3O)_2\underset{\overset{\|}{O}}{P}CH_2CH_2COOCH_3$ | 122 (3) | 1.4370 | 1.2010 | 42.71 | 42.41 | — | — | 52.0 |
| 2 | $(C_2H_5O)_2\underset{\overset{\|}{O}}{P}CH_2CH_2COOC_2H_5$ | 123—124 (3) | 1.4310 | 1.0941 | 56.31 | 56.26 | 13.17 | 13.02 | 39.4 |
| 3 | $(n\text{-}C_4H_9O)_2\underset{\overset{\|}{O}}{P}CH_2CH_2COOC_4H_9\text{-}n$ | 147—149 (4) | 1.4382 | 1.0024 | 84.33 | 84.00 | 9.73 | 9.62 | 26.2 |
| 4 | $(iso\text{-}C_4H_9O)_2\underset{\overset{\|}{O}}{P}CH_2CH_2COOC_4H_9\text{-}iso$ | 163—165 (6) | 1.4360 | 1.0020 | 83.48 | 84.00 | 9.79 | 9.62 | 42.0 |
| 5 | $(CH_3O)_2\underset{\overset{\|}{O}}{P}CH_2\underset{\overset{\|}{CH_3}}{C}HCOOCH_3$ | 126—127 (5) | 1.4372 | 1.1681 | 47.09 | 47.05 | — | — | 56.8 |
| 6 | $(C_2H_5O)_2\underset{\overset{\|}{O}}{P}CH_2\underset{\overset{\|}{CH_3}}{C}HCOOC_2H_5$ | 123—125 (5) | 1.4335 | 1.0761 | 61.09 | 60.90 | 12.32 | 12.28 | 34.1 |
| 7 | $(n\text{-}C_4H_9O)_2\underset{\overset{\|}{O}}{P}CH_2\underset{\overset{\|}{CH_3}}{C}HCOOC_4H_9\text{-}n$ | 153—155 (3) | 1.4390 | 1.0019 | 88.41 | 88.62 | 9.51 | 9.23 | 31.2 |
| 8 | $(iso\text{-}C_4H_9O)_2\underset{\overset{\|}{O}}{P}CH_2\underset{\overset{\|}{CH_3}}{C}HCOOC_4H_9\text{-}iso$ | 155—157 (5) | 1.4375 | 1.9911 | 88.82 | 88.62 | 9.33 | 9.23 | 62.1 |
| 9 | $(C_2H_5O)_2\underset{\overset{\|}{O}}{P}CH_2\underset{\overset{\|}{CH_3}}{C}HCOOCH_3$ | 120—121 (5) | 1.4346 | 1.1021 | 56.46 | 56.26 | 13.11 | 13.02 | 52.8 |

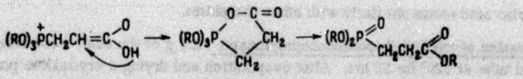
In combining trimethylphosphite with acrylic and methacrylic acids the methyl esters were obtained of β-phosphonopropionic and β-phosphonoisobutyric acids, described earlier by A. N. Pudovik [6]. The ethyl esters of these acids also have constants identical with those described earlier [6, 7]. On saponifying the esters of β-phosphonopropionic acid the acid itself was obtained, earlier described in the literature [8].

The constants of the phosphonocarboxylic esters obtained by us are given in the table.

The union of trialkylphosphites with unsaturated acids probably proceeds through conjugation of the C=C—C=O bonds with subsequent regrouping of hydrogen.



It appears to us also entirely probable that the dipolar ion $(RO)_3\overset{+}{P}CH_2CH=C\langle^{O^-}_{OH}$ at the intermediate stage is stabilized, forming a cyclic addition product, corresponding to the first stage of the Arbuzov rearrangement, with subsequent splitting up:



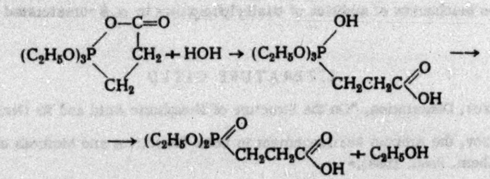
It is possible that the P—O bond in the ring is of ionic character. In favor of the suggested formation of an intermediate unstable addition product the following facts may be cited:

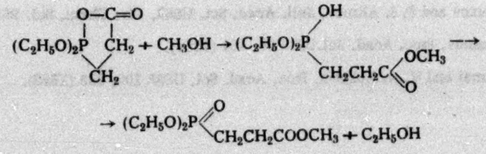
1. In reacting triethylphosphite with methacrylic acid without heating in a sealed tube at room temperature for a considerable time (2-3 weeks) the smell of the initial components disappears, and the test with a copper monohalide indicates the absence of triethylphosphite. The undispersed addition product has $n_D^{20}$ 1.4320, $d_0^{20}$ 0.9957. These constants do not change afterwards (even in two months). On distilling, the ethyl-β-phosphonoisobutyrate is obtained with very low yield (10-15%); and there are signs, during distillation, of decomposition. It may be suggested that, in this case, by heating, the unstable addition product is decomposed.

2. The addition product obtained reacts with water with rise in temperature. The aqueous emulsion quickly disappears; the temperature rises by 15-20°, whereas the distilled β-phosphonoisobutyric ester, under similar conditions, does not react with water.

3. Under the action of methanol on the undispersed addition product there is rise in temperature. By distillation in this case the methyldiethyl-β-phosphonoisobutyrate was separated.

It may be suggested that water and alcohol act on the intermediate product as follows:

1. 

2. 

A final decision on the problem of the mechanism of the reactions we have been studying requires further experimental investigation. But the results so far obtained permit the suggestion that the reaction of unsaturated acids with trialkylphosphites proceeds in accordance with the Arbuzov regrouping scheme. Evidently the action of $\pi,\pi$-conjugated systems on trialkylphosphites may be regarded as one of the exceptional cases of Arbuzov rearrangement.

## EXPERIMENTAL

Addition of trimethylphosphite to acrylic acid. 7 g acrylic acid was added dropwise to 12 g trimethylphosphite. For some time after starting the addition (when about a third of the total amount of acid had been added) a heating up of the reaction mixture began, and temperature quickly rose to 125°. After heat evolution had ceased the mixture was heated at 120° for two hrs. By double distillation 10 g trimethyl-β-phosphonopropionate was obtained.

In a similar manner the reactions of acrylic acid with other phosphites were carried out. The basic constants of the esters thus synthesized are given in the above-mentioned table.

The addition of trimethylphosphite to methacrylic acid. 8.6 g methacrylic acid was added to 12 g trimethylphosphite. On mixing these components the temperature rose by 20°. The mixture was heated at 120-130° for 3 hrs. 9.8 g (56.8%) trimethyl-β-phosphonoisobutyrate was recovered by distillation.

Methacrylic acid reacts similarly with other phosphites.

Saponification of triethyl-β-phosphonopropionate. 2.3 g of the ester was heated with 15% hydrochloric acid in a sealed tube at 120° for 10 hrs. After evaporation and drying a crystalline product was obtained, weighing 1.6 g and, after recrystallization, having a m. p. of 168°.

In the same way the isobutyl ester of β-phosphonoisobutyric acid was saponified. The mixing test showed no depression of m. p.

Action of methanol on the addition product of methacrylic acid with triethylphosphite. 16.6 g of the phosphite and 8.6 g of the acid were left to stand at room temperature in a sealed tube. After a month the mixture had the following constants; $n_D^{20}$ 1.4310, $d_0^{20}$ 0.9961; after 2 months, $n_D^{20}$ 1.4320, $d_0^{20}$ 0.9957. The test with copper monochloride showed no rise in temperature; the phosphite smell had disappeared.

2 g methanol was added to 10.4 g of product. On mixing the temperature rose by 5°. Within two days the product was distilled. After double fractionation 5.3 g methyldiethyl-β-phosphonoisobutyrate was obtained.

Literature data [6]: $n_D^{20}$ 1.4350, $d_0^{20}$ 1.1212.

## SUMMARY

1. A new method has been developed for obtaining phosphonocarboxyl acid esters by addition of trialkylphosphites to α,β-unsaturated acids.

2. The reaction mechanism of addition of trialkylphosphites to α,β-unsaturated acids has been suggested and studied.

## LITERATURE CITED

[1] A. E. Arbuzov, Dissertation, "On the Structure of Phosphoric Acid and Its Derivatives" (Kazan, 1905).

[2] B. A. Arbuzov, the Arbuzov Rearrangement in book "Reactions and Methods of Study of Organic Compounds" (State Chem. Press, 1954).*

[3] A. E. Arbuzov and P. I. Alimov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 268 (1951).

[4] V. S. Abramov, Proc. Acad. Sci.USSR 95, 991 (1954).

[5] Gil'm Kamai and V. A. Kukhtin, Proc. Acad. Sci. USSR 102, 283 (1955).

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* In Russian

[6] A. N. Pudovik, Progr. Chem. (Usp. Khim.) 23, 547 (1954).

[7] A. E. Arbuzov and A. A. Dunin, J. Russ. Phys.-Chem. Soc. 46, 295 (1914).

[8] A. E. Arbuzov, J. Russ. Phys.-Chem. Soc. 59, 239 (1927).

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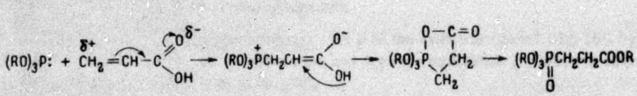
# ADDITION OF COMPLETE ESTERS OF PHOSPHORUS AND PHOSPHONOUS ACIDS TO CONJUGATED SYSTEMS

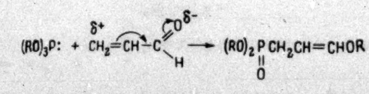
## II. ADDITION OF TRIALKYLPHOSPHITES TO ACROLEIN AND CROTONALDEHYDE

Gil'm Kamai and V. A. Kukhtin

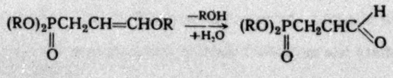
In the previous communication [1] we had described the addition of trialkylphosphites to α, β-unsaturated acids, proceeding, in our opinion, by the scheme



Continuing our investigations in this field, we established that α, β-unsaturated aldehydes are also capable of entering into very active reaction with trialkylphosphites. Thus, for example, triethylphosphite reacts with acrolein with the evolution of heat, in which connection the temperature rises to 70°. However, it proved much more difficult to isolate the reaction product in this case than in the reaction of triethylphosphite with acrylic acid. Only by running the reaction in dioxane solution were we able to isolate the addition product of triethyl phosphite to acrolein. The obtained product contains a double bond, and gives a negative test for the carbonyl group. Its saponification yielded diethylphosphonopropionaldehyde. The results obtained in studying the product, and also the analysis data, indicate that it is the ethyl ester of γ-ethoxyallylphosphonic acid. Consequently, the same as the unsaturated acids, the unsaturated aldehydes add trialkylphosphites to the conjugated system $C=C-C=O$ in the 1–4 position.



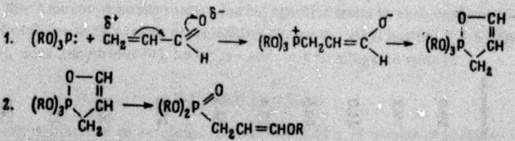
The reaction of acrolein with other phosphites also led to obtaining similar addition products. The saponification of the butyl ester of γ-butoxyallylphosphonic acid gave the butyl ester of phosphonopropionaldehyde.



$$(RO)_2\underset{\overset{\|}{O}}{P}CH_2CH{=}CHOR \xrightarrow[+H_2O]{-ROH} (RO)_2\underset{\overset{\|}{O}}{P}CH_2CHC\overset{H}{\lessdot}{O}$$

Similar to acrolein, crotonaldehyde adds trialkylphosphites, but less vigorously. The reaction is accompanied by only very slight self-heating of the reaction mass at the start, and requires longer additional heating. The constants of the compounds obtained by us are given in the table.

Evidently, the reaction of α, β-unsaturated aldehydes with trialkylphosphites proceeds in a manner similar to the addition of phosphites to unsaturated acids, i. e., by the Arbuzov rearrangement scheme, in two stages.

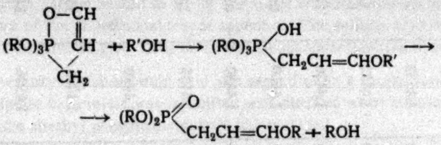


This hypothesis is supported by the action of high temperatures, water, and alcohol on the undistilled addition product. In the experiments performed by us the addition products of trialkylphosphites to acrolein behaved in many respects in the same manner as the earlier described addition products of trialkylphosphites to unsaturated acids.

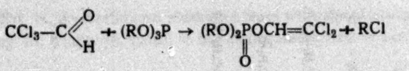
First of all, it is necessary to mention that the first distillation of the addition products is very turbulent and there are indications of strong decomposition. The second distillation proceeds with only slight tarring of the product. The yield of the esters of γ-alkoxyallyphosphonic acid is increased if the addition product is heated to 180-200° prior to distillation.

The temperature rises by 10-15° if the undistilled addition product is treated with water. After some time the addition product is converted into the corresponding phosphonoaldehyde. The distilled esters of the γ-alkoxyallylphosphonic acids are not saponified with pure water under these conditions.

The action of an alcohol on the undistilled addition product results in a temperature rise of 5-6° and an ester is obtained, containing the alcohol radical in the γ-alkoxyallyl group. Thus, the action of methanol on the addition product of triethylphosphite to acrolein gave the ethyl ester of γ-methoxyallylphosphonic acid.

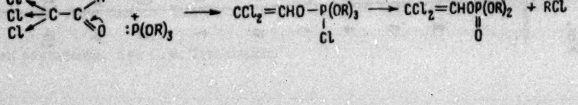


All of these data serve to support our earlier expressed postulation that the reaction of trialkylphosphites with π,π-conjugated systems is a particular case of the Arbuzov rearrangement and proceeds in the same manner as the scheme proposed for the reaction of alkyl halides with trivalent phosphorus compounds. Evidently, not only π,π-conjugated systems, but also systems with σ,π-conjugation are capable of such reaction. The reaction of various σ,π-conjugated systems with trialkylphosphites is described in a number of papers [2-4]. Thus, for example, chloral reacts with trialkylphosphites in the following manner



$$\mathrm{CCl_3{-}C}{\lessdot}^{O}_{H} + \mathrm{(RO)_3P} \rightarrow \mathrm{(RO)_2}\underset{\underset{O}{\|}}{\mathrm{P}}\mathrm{OCH{=}CCl_2} + \mathrm{RCl}$$

The authors of these papers have different explanations for such an "anomalous" reaction course. We are of the opinion that the most probable explanation for such reactions is obtained if we consider the haloaldehydes and haloketones to be σ,π-conjugated systems. Thus, for example, chloral, by analogy with π,π-conjugated systems, should react by the scheme



| Expt. Nos. | Formula | Boiling point (pressure in mm) | $n_D^{20}$ | $d_0^{20}$ | $MR_D$ |  | Percent phosphorus |  | Yield (in %) |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | found | calculated | found | calculated |  |
| 1 | $(CH_3O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOCH_3$ | 125—126 (8) | 1.4432 | 1.1570 | 41.33 | 40.79 | 16.8 | 17.2 | 30.0 |
| 2 | $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOC_2H_5$ | 132—134 (3) | 1.4442 | 1.0603 | 55.81 | 55.75 | 13.8 | 13.9 | 19.2 |
| 3 | $(n\text{-}C_3H_7O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOC_3H_7\text{-}n$ | 153—155 (5) | 1.4426 | 1.0089 | 69.54 | 69.67 | 11.4 | 11.7 | 11.0 |
| 4 | $(n\text{-}C_4H_9O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOC_4H_9\text{-}n$ | 156—157 (3) | 1.4460 | 0.9806 | 82.94 | 83.52 | 10.4 | 10.1 | 40.6 |
| 5 | $(iso\text{-}C_4H_9O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOC_4H_9\text{-}iso$ | 150—151 (3) | 1.4430 | 0.9750 | 83.16 | 83.52 | 9.8 | 10.1 | 17.4 |
| 6 | $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH{=}CHOCH_3$ | 123—124 (3) | 1.4435 | 1.0985 | 52.08 | 51.76 | 14.5 | 14.9 | 34.5 |
| 7 | $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH_2C\genfrac{}{}{0pt}{}{\diagup O}{\diagdown H}$ | 128—130 (4) | 1.4480 | 1.1320 | 45.86 | 45.83 | 15.8 | 15.9 | 25.5 |
| 8 | $(n\text{-}C_4H_9O)_2\underset{\underset{O}{\Vert}}{P}CH_2CH_2C\genfrac{}{}{0pt}{}{\diagup O}{\diagdown H}$ | 150—151 (5) | 1.4406 | 1.0129 | 65.16 | 63.88 | 12.0 | 12.4 | 30.8 |
| 9 | $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}\underset{\underset{CH_3}{\vert}}{C}HCH{=}CHOC_2H_5$ | 136—138 (1) | 1.4506 | 1.0436 | 60.89 | 60.43 | 12.3 | 13.1 | 17.1 |
| 10 | $(n\text{-}C_3H_7O)_2\underset{\underset{O}{\Vert}}{P}\underset{\underset{CH_3}{\vert}}{C}HCH{=}CHOC_3H_7\text{-}n$ | 152—154 (3) | 1.4496 | 1.0046 | 74.29 | 74.28 | 11.0 | 11.1 | 12.9 |

Pudovik and Lebedeva [4] give nearly the same scheme for similar reactions. It is quite probable that the general mechanism of the Arbuzov rearrangement, having specific traits in each individual case, lies at the base of many reactions of phosphites with various electrophilic reagents: alkyl halides [5], inorganic [6] and organic [7] acids, aldehydes [8], acid anhydrides [9], and $\pi,\pi$- and $\sigma,\pi$-conjugated systems.

## EXPERIMENTAL

Addition of trimethylphosphite to acrolein. A solution of 10 g of trimethylphosphite in dioxane was treated with 4.5 g of acrolein. After half of the acrolein had been added the temperature had risen to 52°: with further addition of the acrolein, done with cooling of the reaction mixture in a water bath, the temperature gradually rose to 92°. The reaction mass was heated for 2.5 hrs at 80-90°, after which the reaction was considered to be done. After removal of the dioxane the reaction mixture was distilled. Much decomposition occurred during the distillation and the yield of product was very low. The yield can be raised up to 30% if the product is treated with methyl alcohol prior to distillation. The amount of alcohol added was 2.6 g, and the reaction mass was allowed to stand for a day at room temperature.

This treatment gave the methyl ester of $\gamma$-methoxyallylphosphonic acid (see the table for constants and analysis data).

The other addition products of trialkylphosphites to acrolein were obtained in a similar manner. The reactions with the propyl and butyl phosphites were run without solvent. In the case of the tri-n-butylphosphite the yield of product was increased from 18 to 40% if the reaction mass was treated with butanol prior to distillation.

Action of methanol on the addition product of triethylphosphite to acrolein. To 15 g of undistilled addition product was added 2.13 g of methanol. The temperature during the addition of the methanol rose 8°. After two days the reaction mixture was distilled to give 4.2 g of the ethyl ester of $\gamma$-methoxyallylphosphonic acid.

Saponification of the n-butyl ester of $\gamma$-butoxyallylphosphonic acid. To 5.5 g of the ester was added 0.4 ml of 2% sulfuric acid solution. When heated to 70-80° the water emulsion quickly disappeared, and the odor of butanol and the sharp odor of the phosphonoaldehyde appeared. The sulfuric acid was neutralized with soda, after which the product was distilled to give 1.5 g of dibutyl phosphonopropionaldehyde.

The ethyl ester of $\gamma$-ethoxyallylphosphonic acid was saponified in a similar manner. The undistilled addition product of triethylphosphite to acrolein was saponified with distilled water at room temperature, in which connection a 31% yield of the diethyl phosphonoaldehyde was obtained.

Addition of triethylphosphite to crotonaldehyde. To 17 g of the phosphite was added 7 g of crotonaldehyde. The temperature rose 10°. The reaction mass was heated at 110° for 2 hrs. The yield of addition product after distillation was 4.7 g.

The reaction of tripropylphosphite with crotonaldehyde was run in a similar manner.

## SUMMARY

1. The addition of trialkylphosphites to $\alpha,\beta$-unsaturated aldehydes was studied.

2. It was established that $\alpha,\beta$-unsaturated aldehydes react with phosphites in the same manner as do $\alpha,\beta$-unsaturated acids, adding the trialkylphosphite to the conjugated system of double bonds.

## LITERATURE CITED

[1] Gil'm Kamai and V. A. Kukhtin, J. Gen. Chem. 27, 2372 (1957).*

[2] W. Perkow, Chem. Ber. 87, 755 (1954).

[3] F. Allen and O. Janson, J. Am. Chem. Soc. 77, 2871 (1955).

[4] A. N. Pudovik and N. M. Lebedeva, Proc. Acad. Sci. USSR 101, 889 (1955).

[5] A. E. Arbuzov, Dissertation: The Structure of Phosphorus Acid and Its Derivatives (Kazan, 1905).

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* Original Russian pagination. See C.B. Translation.

[6] A. E. Arbuzov and P. I. Alimov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 268.

[7] Gil'm Kamai, V. A. Kukhtin, and O. D. Strogova, Trans. Kazan Chem.-Techn. Inst. 1956, No. 21, 155.

[8] V. S. Abramov, Proc. Acad. Sci. USSR 95, 991 (1954).

[9] Gil'm Kamai and V. A. Kukhtin, Proc. Acad. Sci. USSR 102, 283 (1955).

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# MIXED ESTERS OF 1,1,1-TRICHLORO-TERT-BUTYLPHOSPHITE, III

V. S. Abramov and V. K. Khairullin

In previous papers we had communicated on the reactions of the chloride of bis(1,1,1-trichloro-tert-butyl) phosphite [1] and the chloride of 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexylphosphite [2] with various alcohols. It was shown that the chloride of bis(1,1,1-trichloro-tert-butyl) phosphite, when reacted with primary and secondary alcohols and phenol, in the presence of pyridine in anhydrous ether medium, gives the corresponding mixed phosphite esters. However, we were unable to obtain the complete phosphite esters with tertiary alcohols. In contrast to the indicated chloride, under similar conditions the chloride of 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexylphosphite gives mixed esters only with primary alcohols of normal and iso structure, and does not give mixed esters with secondary and tertiary alcohols, or with phenol.

The present work is a continuation of the investigation started by us to study the formation of complete phosphite esters from tertiary alcohols. The cyclic phosphite esters are definitely of interest, especially those obtained from ditertiary glycols. A. E. Arbuzov and his students [3] synthesized the esters of tetramethylethylene glycol phosphite, di-1,1'-cyclohexanediol phosphite and pyrocatechol phosphite. The mixed esters of the indicated acids and tertiary alcohols were not studied by the authors.

We studied the reaction of various glycols: ethylene glycol, propylene glycol, tetramethylethylene glycol and pyrocatechol with the dichloride of 1,1,1-trichloro-tert-butylphosphite, in the presence of pyridine (in anhydrous ether medium), reacts with the indicated glycols and pyrocatechol and gives the corresponding 1,1,1-trichloro-tert-butyl esters of various glycol phosphites. Special mention must be made of the formation of the 1,1,1-trichloro-tert-butyl ester of tetramethylethylene glycol phosphite, for the reason that in this case we have a complete ester with tertiary radicals. A similar successful result is also obtained with pyrocatechol. It is apparently impossible to synthesize phosphites with tertiary aliphatic groups due to steric hindrance. The synthesis of the tertiary esters of tetramethylethylene glycol phosphite and pyrocatechol phosphite proceeds without any difficulties whatsoever. The ease with which these esters are formed must be explained as being due to the sterically favorable ring structure of the ester. A study of the fine structure of these esters by physical methods is of definite interest.

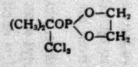
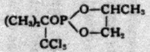
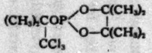
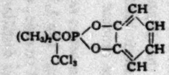
However, the dichloride of 1,1,1-trichloro-tert-butylphosphite, in the presence of pyridine (in either benzene or dioxane medium), when heated to 100°, does not react with benzopinacol and does not give the corresponding ester. It is quite probable that benzopinacol possesses a bulkier spatial structure. The phosphite esters are not obtained immediately when steric hindrance factors begin to operate. In both cases the benzopinacol was recovered unchanged (70% of the amount taken for reaction) from the reaction products.

The obtained cyclic phosphite esters represent syrupy, colorless, clear liquids, having a weak phosphite odor, and soluble in organic solvents. The 1,1,1-trichloro-tert-butyl ester of tetramethylethylene glycol phosphite, after vacuum-distillation and storage, crystallized as colorless needles. The 1,1,1-trichloro-tert-butyl ester of pyrocatechol phosphite, after distillation, crystallized so rapidly that it proved impossible to determine its constants in the liquid state. The obtained cyclic esters are listed in Table 1.

Along the way we studied the reaction of the dichloride of 1,1,1-trichloro-tert-butylphosphite with aliphatic alcohols. The reaction was run in the same manner as indicated above. The primary alcohols – methyl, ethyl and n-butyl – readily react with the dichloride under the designated conditions to yield the corresponding mixed phosphite esters. The esters represent clear syrupy liquids with an odor reminiscent of triethylphosphite. The constants of the esters are listed in Table 2 (nos. 1-3).

TABLE 1

Constants of 1,1,1-Trichloro-tert-butyl Esters of Glycol Phosphites

| Expt. Nos. | Formula of obtained compounds | Boiling point | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ |  | Yield (in %) | % Cl |  | % P |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | found | calculated |  | found | calculated | found | calculated |
| 1 |  | 104° (5 mm) | 1.4226 | 1.4980 | 54.74 | 55.38 | 62.5 | 39.82 | 39.77 | 11.48 | 11.58 |
| 2 |  | 97 (1 mm) | 1.3665 | 1.4891 | 59.47 | 60.05 | 60.0 | 37.70 | 37.78 | 11.01 | 11.01 |
| 3 |  | 122—123 (3 mm)* | 1.2635 | 1.4830 | 73.15 | 73.90 | 56.2 | 32.70 | 32.87 | 9.60 | 9.58 |
| 4 |  | 151 (6 mm)** | — | — | — | — | 95.0 | 33.67 | 33.71 | 9.72 | 9.82 |

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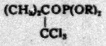
* M. p. 60-61°.

** M. p. 62-63°.

TABLE 2

Constants of Mixed Esters of Phosphorus Acid  $(CH_3)_2C(CCl_3)OP(OR)_2$

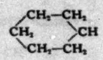
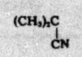
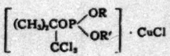
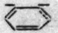
| Expt. Nos. | R | Boiling point at pressure (in mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ |  | Yield (in %) | % Cl |  | % P |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | found | calculated |  | found | calculated | found | calculated |
| 1 | $CH_3$ | 106° (9) | 1.3346 | 1.4779 | 57.15 | 57.58 | 79.2 | 39.22 | 39.47 | 11.38 | 11.50 |
| 2 | $C_2H_5$ | 90 (1) | 1.2898 | 1.4700 | 66.43 | 66.81 | 75.0 | 35.60 | 35.75 | 10.27 | 10.41 |
| 3 | n-$C_4H_9$ | 123—124 (1) | 1.1611 | 1.4675 | 84.60 | 85.29 | 62.2 | 29.90 | 30.08 | 8.84 | 8.75 |
| 4 | iso-$C_3H_7$ | 98 (1.5) | 1.1872 | 1.4632 | 75.57 | 76.05 | 75.6 | 32.51 | 32.67 | 9.30 | 9.51 |
| 5 | $(CH_2Cl)_2CH$ | 194—197 (3) | 1.4730 | 1.5132 | 94.80 | 95.52 | 58.0 | 53.60 | 53.56 | 6.68 | 6.69 |
| 6 |  | 183—184 (3) | 1.2105 | 1.4985 | 98.35 | 99.36 | 70.0 | 26.20 | 26.21 | 7.54 | 7.65 |
| 7 | $C_6H_5$ | 189—190 (2) | 1.3130 | 1.5640 | 97.51 | 96.56 | 78.0 | 27.17 | 27.01 | 7.89 | 7.87 |
| 8 |  $(CH_3)_2C(CN)$ | 163 (1) | 1.2533 | 1.4776 | 84.76 | 84.82 | 61.4 | 28.40 | 28.32 | 8.52 | 8.25 |

TABLE 3

Complexes of Mixed Phosphites with Cuprous Chloride 

$\left[(CH_3)_2\underset{CCl_3}{\underset{|}{C}}OP\begin{matrix}OR\\OR'\end{matrix}\right]\cdot CuCl$

| Expt. Nos. | R | R′ | Temperature on mixing rose by | Recrystallization solvent | Melting point | % Cl |  | % P |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | found | calcu-lated | found | calcu-lated |
| 1 | $-(CH_2)_2-$ |  | 28° | — |  | Glassy mass |  |  |  |
| 2 | $-\underset{CH_3}{\underset{\vert}{CH}}-CH_2-$ |  | 30 | — |  | Glassy mass |  |  |  |
| 3 | $-C(CH_3)_2-C(CH_3)_2-$ |  | 12 | Chloroform + anhydrous alcohol (1 : 1) | 174—175° | 33.42 | 33.56 | 7.25 | 7.33 |
| 4 |  |  | 3 | Chloroform + ligroin (4 : 1) | 146 (decomp.) | 34.07 | 34.21 | 7.59 | 7.79 |
| 5 | $CH_3$ | $CH_3$ | 35 | Anhydrous alcohol | 157—158 (decomp.) | 38.34 | 38.49 | 8.31 | 8.41 |
| 6 | $C_2H_5$ | $C_2H_5$ | 50 | — |  | Thick sirup |  |  |  |
| 7 | n-$C_4H_9$ | n-$C_4H_9$ | 44 | — |  | Thick sirup |  |  |  |
| 8 | iso-$C_3H_7$ | iso-$C_3H_7$ | 18 | Anhydrous alcohol | 144—144.5 | 33.20 | 33.40 | 7.18 | 7.31 |
| 9 | $(CH_2Cl)_2CH$ | $(CH_2Cl)_2CH$ | 46 | — |  | Thick sirup |  |  |  |
| 10 | $C_6H_{11}$ | $C_6H_{11}$ | 5 | Chloroform + methanol (1 : 9) | 160—161 | 28.02 | 28.15 | 6.01 | 6.15 |
| 11 | $C_6H_5$ | $C_6H_5$ | 7 | Chloroform + anhydrous alcohol (1 : 4) | 121—122 | 28.59 | 28.79 | 6.13 | 6.29 |
| 12 | $(CH_3)_2\underset{CN}{\underset{\vert}{C}}$ | $(CH_3)_2\underset{CN}{\underset{\vert}{C}}$ | 0 | Chloroform + methanol (1 : 1) | 148 | 29.70 | 29.82 | 6.51 | 6.53 |

The secondary alcohols — isopropyl, α,γ-dichlorohydrin, glycerol and cyclohexanol — also readily react with the dichloride in the presence of pyridine and give the corresponding mixed esters (Table 2, Nos. 4-6). Phenol, with the dichloride, gives a mixed ester that distills without decomposition (Table 2, No. 7). The yields of the esters ranged from 62 to 79%.

Of special interest was the reaction of the dichloride of 1,1,1-trichloro-tert-butylphosphite with tertiary alcohols. Trimethylcarbinol, acetone cyanohydrin, 1-trichloromethyl-1-cyclohexanol and triphenylcarbinol all react differently with the dichloride. Only the acetone cyanohydrin smoothly gives the corresponding complete mixed phosphite ester in a yield of 61.4% (Table 2, No. 8). The formation of the complete mixed phosphite ester can be explained by the structure specificity of the nitrile group. In contrast to other radicals, each having three δ-bonds, directed toward the tetrahedron, and labile π-bonds, the carbon atom of the nitrile group has one δ-bond, which makes it possible to regard acetone cyanohydrin as belonging rather to the class of secondary alcohols.

Trimethylcarbinol with the dichloride in the presence of pyridine (in anhydrous ether medium) liberates the theoretical amount of pyridine hydrochloride and gives the mixed tert-butyl-1,1,1-trichloro-tert-butylphosphite. The mixed acid ester reacts with aldehydes and ketones [4] and gives the corresponding esters of α-hydroxyalkylphosphonic acids. It proved impossible to isolate any other products.

Triphenylcarbinol with the dichloride in the presence of pyridine (in anhydrous 70-120° ligroin medium) at 45-50° gives about 50% of pyridine hydrochloride and some triphenylchloromethane (45%, based on taken triphenylcarbinol). We were unable to isolate the mixed phosphite ester.

1-Trichloromethyl-1-cyclohexanol with the dichloride gives, instead of the expected complete ester, the chloride of the mixed ester 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexylphosphite in good yield and some unchanged 1-trichloromethyl-1-cyclohexanol [2]. Such a reaction course is evidently determined by the stability of the OH group.

The dichloride of 1,1,1-trichloro-tert-butylphosphite in its reactions with alcohols shows the same behavior pattern as had been observed in our earlier [1, 2] investigations: primary and secondary alcohols readily react with the dichloride and give the corresponding mixed phosphites, whereas the phosphites are not obtained with tertiary carbinols. Steric hindrance increases in going from the primary alcohols to the tertiary and it is possible that this plays an important role, together with the relative reactivity of the alcohols, in the formation of the phosphites.

All of the mixed esters of phosphorus acid react with cuprous chloride [5] and in most cases give well formed crystalline products; others, as can be seen from the data in Table 3, are either syrupy liquids or glassy products.

## EXPERIMENTAL

Preparation of mixed esters of phosphorus acid. Into a one-liter three-necked flask, fitted with thermometer, dropping funnel, mechanical stirrer and reflux condenser, sealed with a calcium chloride tube, was charged 0.2 mole of glycol or 0.4 mole of alcohol and 0.4 mole of pyridine in 300-400 ml of anhydrous ether. The flask was cooled with an ice-salt mixture. To the mixture with vigorous stirring at 0-5° was added in drops 0.2 mole of the dichloride of 1,1,1-trichloro-tert-butylphosphite. After all of the chloride had been added the stirring was continued, at first at room temperature, and then with heating to ether boil. The precipitate of pyridine hydrochloride was filtered rapidly, the ether was distilled off, and the residue was vacuum-distilled. Usually two successive distillations were sufficient to give a pure mixed ester; rarely did we limit ourselves to one distillation due to the decomposition that occurred here (Table 2, No. 5). The properties of the esters are listed in Tables 1 and 2.

Preparation of complexes of mixed esters of phosphorus acid with cuprous chloride. To 3-7 g of the phosphite, contained in a test tube, was added the calculated amount of cuprous chloride. The mixture was stirred with a thermometer, and the rise in temperature was observed. Then the mixture was heated until almost all of the cuprous chloride had dissolved. In most cases after cooling the whole congealed into a crystalline mass or it remained as a thick (up to a hard) syrup, and then it was recrystallized.

The complexes of the mixed phosphites with cuprous chloride are characterized in Table 3.

## SUMMARY

1. It was shown that the dichloride of 1,1,1-trichloro-tert-butylphosphorus acid readily reacts with glycols and primary and secondary alcohols, and gives mixed esters of phosphorus acid. Phosphites are not formed when tertiary alcohols are used. As an exception to this rule we obtained the mixed phosphite with acetone cyanohydrin and failed to obtain it with benzopinacol. The indicated reaction courses can be explained as being due to steric hindrance, which increases in going from primary to tertiary alcohols.

The formation of cyclic phosphites with tertiary radicals is explained by the sterically favorable ring structure, except that the reaction does not go when the structure is made more complex (benzopinacol).

2. Twelve mixed esters of phosphorus acid were synthesized, which react with cuprous chloride and give complexes; most of the complexes were isolated as well formed crystals.

## LITERATURE CITED

[1] V. S. Abramov and V. K. Khairullin, J. Gen. Chem. 27, 444 (1957).*

[2] V. S. Abramov and V. K. Khairullin, J. Gen. Chem. 27, 1365 (1957).*

[3] A. E. Arbuzov and M. M. Azanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 544; 1949, 473; A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1950, 529.

[4] V. S. Abramov, Proc. Acad. Sci. USSR 73, 487 (1950).

[5] A. E. Arbuzov, Structure of Phosphorus Acid and Its Derivatives (St. Petersburg, 1905).**

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* Original Russian pagination. See C.B. Translation.

** In Russian.

# REACTION OF DIALKYLPHOSPHITES WITH ALDEHYDES AND KETONES

## XIV. 1,1,1-TRICHLORO-TERT-BUTYL 1-TRICHLOROMETHYLCYCLOHEXYL ESTERS OF SUBSTITUTED α-HYDROXYMETHYLPHOSPHONIC ACID

V. S. Abramov and V. K. Khairullin

We had communicated earlier that bis(1,1,1- trichloro-tert-butyl)phosphite adds at room temperature to the carbon—oxygen bond of the carbonyl group of aldehydes and ketones [1]. The reaction goes without a catalyst. The nature of the reaction in the absence of a catalyst we explain as being due to tautomeric equilibrium of the bis(1,1,1-trichloro-tert-butyl)phosphite forms, the presence of negative chlorine atoms in the molecule making the enol form stable. As the enol form reacts with the carbonyl compound the equilibrium shifts.

In this paper we describe the condensation of 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexylphosphite with aldehydes and ketones. The synthesis and properties of the starting mixed phosphite were described earlier [2]. The condensation of this acid ester with aldehydes and ketones proceeds in the same manner as does the condensation of bis(1,1,1-trichloro-tert-butyl)phosphite without a catalyst.

## EXPERIMENTAL

For practical reasons the condensations were run in small ampuls, in which an equimolar mixture of the acid ester and carbonyl compound was sealed. The reaction mixture was heated for a short time at 50-60° to dissolve the acid ester in the carbonyl compound, and then it was allowed to stand at room temperature. In some cases even during cooling or after the lapse of some time, crystals of the α-hydroxyalkylphosphonic acid esters appeared, the amount of which increased with time. The products of the condensation of chloral and p-tolualdehyde with the acid ester were obtained as viscous, syrupy liquids, which, dissolved in alcohol, formed rectilinear tablets. The condensation of benzaldehyde and of p-nitrobenzaldehyde with the acid ester proceeded with the formation of individual crystals of the esters, and then the mixture congealed into a glass-like mass. Recrystallization of the latter from alcohol gave the α-hydroxyalkylphosphonic acid esters as well defined prismatic crystals.

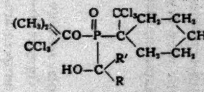
A good solvent for the recrystallization of all of the obtained 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexyl esters of substituted α-hydroxymethylphosphonic acid is alcohol. The ester of α-hydroxycyclohexylphosphonic acid was recrystallized from a mixture of chloroform and methanol (1:5). The esters represent colorless, well formed crystals, without odor, practically insoluble in water, and readily soluble in the common organic solvents: acetone, chloroform, alcohol, ether, dioxane, etc. The nature of the reaction with time, and the physical constants of the obtainedesters, together with their analyses, are presented in the table.

## SUMMARY

1. It was established that the condensation of the mixed ester 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexylphosphite with aldehyde and ketones proceeds without a catalyst, either with slight warming or at room temperature. The nature of the reaction course can be explained by the presence of the enol form of the acid ester, which is stabilized by the negative chlorine atoms present in the molecule.

2. Twelve new 1,1,1-trichloro-tert-butyl-1-trichloromethylcyclohexyl esters of substituted α-hydroxymethylphosphonic acid were synthesized.

1,1,1-Trichloro-tert-butyl-1-trichloromethylcyclohexyl Esters of Substituted α-Hydroxymethylphosphonic Acid



| Expt. Nos. | Reacting carbonyl compound | R | R′ | Reaction time (in hours) | Time before the first crystals of the ester appear (in hours) | Amount of solvent used to recrystallize the ester (in %) | Melting point | Yield (in %) | Chlorine content (in %) * |  | Phosphorus content (in %) * |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  | found | calc. | found | calc. |
| 1 | Acetaldehyde | H | $CH_3$ | 110 | 11 | 100 | 179—181° | 60.0 | 43.69 | 43.86 | 6.32 | 6.39 |
| 2 | Propionaldehyde | H | $C_2H_5$ | 38 | 3.5 | 70 | 178—180 | 61.8 | 42.54 | 42.63 | 6.22 | 6.21 |
| 3 | Butyraldehyde | H | n-$C_3H_7$ | 38 | 3 | 80 | 156—158 | 49.0 | 41.65 | 41.46 | 5.85 | 6.04 |
| 4 | Isovaleraldehyde | H | iso-$C_4H_9$ | 38 | 1 | 90 | 177—178 | 53.0 | 40.44 | 40.36 | 5.66 | 5.88 |
| 5 | Chloral | H | $CCl_3$ | 24 | — | 96 | 162.5 | 46.0 | 54.07 | 54.24 | 5.20 | 5.26 |
| 6 | Benzaldehyde | H | $C_6H_5$ | 36 | 2.75 | 90 | 144—146 | 69.5 | 38.77 | 38.89 | 5.47 | 5.65 |
| 7 | p-Tolualdehyde | H | p-$CH_3C_6H_4$ | 36 | — | 96 | 150—152 | 64.5 | 37.90 | 37.91 | 5.35 | 5.52 |
| 8 | m-Nitrobenzaldehyde | H | m-$NO_2C_6H_4$ | 40 | 14 | 96 | 154—156 | 59.0 | 35.69 | 35.94 | 5.11 | 5.23 |
| 9 | Acetone | $CH_3$ | $CH_3$ | 120 | 2.75 | 96 | 145—147 | 24.0 | 42.47 | 42.63 | 6.14 | 6.21 |
| 10 | α,γ-Dichloroacetone | $CH_2Cl$ | $CH_2Cl$ | 296 | 8 | 96 | 168—168.5 | 69.5 | 49.84 | 49.95 | 5.33 | 5.45 |
| 11 | Cyclopentanone | $-(CH_2)_4-$ |  | 318 | 2 | 96 | 190(decom.) | 8.0 | 40.38 | 40.52 | 5.81 | 5.90 |
| 12 | Cyclohexanone | $-(CH_2)_5-$ |  | 264 | 4 | Chloroform + methanol (1 : 5) | 166—167.5 | 55.5 | 39.35 | 39.46 | 5.73 | 5.75 |

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* The given content of chlorine and phosphorus represents the average of two determinations.

## LITERATURE CITED

[1] V. S. Abramov and V. K. Khairullin, J. Gen. Chem. 26, 811 (1956).*

[2] V. S. Abramov and V. K. Khairullin, J. Gen. Chem. 27, 2381 (1957).*

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* Original Russian pagination. See C.B. Translation.

# DERIVATIVES OF ALKYLPHOSPHONOUS AND PHOSPHONIC ACIDS

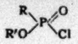
## VI. HALIDES AND ALKYLATED AMIDES OF ALKYLALKOXYPHOSPHONIC ACIDS*

A. I. Razumov, O. A. Mukjacheva, and E. A. Markovich

The complete chlorides of primary phosphonic acids of type $RP(O)Cl_2$ and $ArP(O)Cl_2$ have been known for a long time. The first methods for their preparation, developed by Michaelis [1, 2], Hofmann [3] and Guichard [4], were improved and expanded upon later [5]. Similar chlorides with unsaturated radicals were synthesized later [6-8]. As regards the incomplete chlorides of primary phosphonic acids, they are only slightly known [9, 10].

We were mainly interested in the incomplete chlorides of type $RP(O)\langle^{Cl}_{OR'}$, which could serve as starting compounds for the preparation of the alkylated amides of alkylalkoxyphosphonic acids. These latter compounds, in our opinion, might prove to be biologically active substances.

TABLE 1



| Substance Nos. | Value of |  | Boiling point; pressure (in mm) | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ |  | Analysis for Cl (in %) |  | Yield (in %) |
|---|---|---|---|---|---|---|---|---|---|---|
|  | R | R′ |  |  |  | calc. | found | calc. | found |  |
| 1 | $C_2H_5$ | $C_2H_5$ | 73—74° (10) | 1.1631 | 1.4338 | 35.03 | 34.95 | 22.68 | 22.90,<br>22.80 | 80 |
| 2 | $C_2H_6$ | n- $C_3H_7$ | 85—87 (11—12) | 1.1303 | 1.4400 | 39.75 | 39.76 | 20.82 | 21.15 | 80 |
| 3 | $C_2H_5$ | iso-$C_3H_7$ | 76.5—78.5 (9.5) | 1.1033 | 1.4296 | 39.75 | 39.90 | 20.82 | 20.68,<br>20.60 | 45 |
| 4 | $C_2H_5$ | n- $C_4H_9$ | 100—102 (10—11) | 1.0993 | 1.4395 | 44.36 | 44.19 | 19.24 | 19.33,<br>19.21 | 70 |
| 5 | $C_2H_5$ | iso-$C_4H_9$ | 98—99.5 (13.5) | 1.0898 | 1.4355 | 44.36 | 44.22 | 19.24 | 19.40,<br>19.25 | 70 |
| 6 | $CH_3$ | iso-$C_3H_7$ | 36—37 (0.5) | 1.2924 | 1.4346 | — | — | 22.68 | 22.80,<br>22.65 | 60 |

An attempt to prepare the chlorides from the esters of alkylphosphonic acids by the method of chlorinating with phosphorus pentachloride under the usual conditions, or by means of thionyl chloride, proved unsuccessful. In the first case we obtained as byproduct the complete chlorides $RP(O)Cl_2$ in amounts ranging from 10 to 30 %. The close proximity of the boiling points of the latter makes it extremely difficult to isolate the desired products completely pure. In the second case the yields do not exceed 40% of the theoretical. Only by using a 10-fold amount of solvent in the chlorination of the alkylphosphonates with phosphorus pentachloride at a temperature of 28-30° were we able to obtain the desired compounds with a high degree of purity in yields up to 80% [11] (Table 1).

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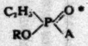
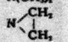
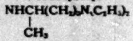
* Presented at the First All-Union Conference on the Chemistry and Use of Organic Phosphorus Compounds (December, 1955, Kazan).

TABLE 2

Derivatives of Ethylphosphonic Acid 

| Substance Nos. | Value of |  | Boiling point; pressure (in %) | $d_4^{20}$ | $n_D^{20}$ | Analysis for P (in %) |  | Yield (in %) |
|---|---|---|---|---|---|---|---|---|
|  | R | A |  |  |  | calculated | found |  |
| 1 | $CH_3$ | $N(C_2H_5)_2$ | 87—87.5° (4) | 1.0043 | 1.4381 | 17.32 | 17.25 | 58 |
| 2 | $C_2H_5$ | $N(C_2H_5)_2$ | 98—98.5 (3.5) | 0.9866 | 1.4355 | 16.10 | 16.30 | 56 |
| 3 | $n-C_3H_7$ | $N(C_2H_5)_2$ | 98—99 (2) | 0.9783 | 1.4368 | 14.98 | 15.08, 15.11 | 33 |
| 4 | $iso-C_3H_7$ | $N(C_2H_5)_2$ | 87—88.5 (0.5) | 0.9650 | 1.4381 | 14.98 | 15.07, 14.90 | 46 |
| 5 | $n-C_4H_9$ | $N(C_2H_5)_2$ | 98.5—99.5 (1) | 0.9562 | 1.4390 | 14.02 | 13.80, 13.91 | 76 |
| 6 | $iso-C_4H_9$ | $N(C_2H_5)_2$ | 95.5—97 (1) | 0.9553 | 1.4357 | 14.02 | 14.32, 14.27 | 35 |
| 7 | $n-C_6H_{13}$ | $N(C_2H_5)_2$ | 116.5—118 (0.5) | 0.9425 | 1.4417 | 12.58 | 12.45, 12.54 | 12 |
| 8 | $C_5H_{11}$ | $N(C_2H_5)_2$ | 118—120.5 (0.5) | 1.0066 | 1.4630 | 12.55 | 12.63, 12.41 | 15 |
| 9 | $C_6H_5CH_2$ | $N(C_2H_5)_2$ | 162—163 (2) | 1.0554 | 1.4975 | 12.06 | 12.15, 12.04 | 25 |
| 10 | $C_2H_5$ | $NHC_2H_5$ | 111.5—112 (2.5) | 1.0232 | 1.4380 | 18.76 | 18.91, 18.78 | 27 |
| 11 | $iso-C_4H_9$ | $NHC_2H_5$ | 129—129.5 (1) | 0.9749 | 1.4358 | 16.06 | 15.95, 15.82 | 73 |
| 12 | $C_2H_5$ | $N(CH_3)_2$ | 63—64 (0.5) | 1.0100 | 1.4305 | 18.78 | 18.87, 19.12 | 76 |
| 13 | $C_2H_5$ |  | 89—92 (1.5) | 1.0752 | 1.4488 | 19.01 | 18.88, 19.14 | 60 |
| 14 | $C_2H_5$ | $NHCH_2CH_2Cl$ | 144—145 (0.75) | 1.1515 | 1.4565 | 15.54 | 15.04, 15.16 | 52 |
| 15 | $C_2H_5$ |  $NH\underset{\overset{\vert}{CH_3}}{C}H(CH_2)_3N(C_2H_5)_2$ | 153—154 (0.25) | 0.9594 | 1.4530 | 11.15 | 10.94, 10.81 | 61 |
| 16 | $p-NO_2-C_6H_4$ | $N(C_2H_5)_2$ | 172.5 (0.8) | 1.1861 | 1.5309 | 10.83 | 10.65, 10.72 | 55 |
| 17 | $C_2H_5$ | $N(C_2H_5)_2$ | 106—108 (2) | 1.0297 | 1.4802 | 14.83 | 14.60, 14.68 | 52 |

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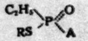
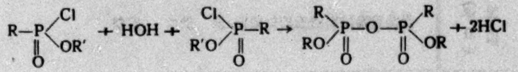
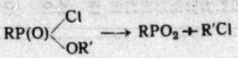
* Formula of substance No. 17 

The synthesized chlorides are liquids that are easily hydrolyzed even in the air. When treated with water in the presence of a base they form esters of pyrophosphonic acids.



$$R{-}P(O)(Cl)(OR') + HOH + (Cl)(R'O)P(O){-}R \rightarrow (R)(RO)P(O){-}O{-}P(O)(R)(OR) + 2HCl$$

Thermally the chlorides are also quite unstable, showing a tendency to decompose in accord with the scheme

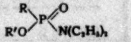


$$RP(O)(Cl)(OR') \longrightarrow RPO_2 + R'Cl$$

Reaction of the obtained chlorides with amines gave the corresponding alkylated amides of alkylalkoxyphosphonic acids (Tables 2 and 3).

TABLE 3

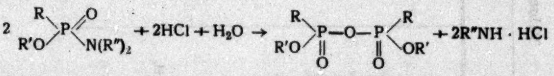
Derivatives of Methyl- and Isopropylphosphonic Acids



$$(R)(R'O)P(=O)N(C_2H_5)_2$$

| Substance Nos. | Value of |  | Boiling point; pressure (in mm) | $d_4^{20}$ | $n_D^{20}$ | Analysis for P (in %) |  | Yield (in %) |
|---|---|---|---|---|---|---|---|---|
|  | R | R′ |  |  |  | calc. | found |  |
| 1 | $CH_3$ | $CH_3$ | 71—74 (0.5) | 1.0214 | 1.4355 | 18.78 | 18.58,<br>18.57 | 50 |
| 2 | $CH_3$ | $C_2H_5$ | 77—79 (1.5) | 0.9944 | 1.4350 | 17.31 | 17.18,<br>17.11 | 50 |
| 3 | $CH_3$ | iso – $C_3H_7$ | 80—81.5 (0.1) | 1.0763 | 1.4395 | 16.06 | 16.43,<br>16.49 | 41 |
| 4 | iso –$C_3H_7$ | $C_2H_5$ | 74.5—75 (0.5) | 0.9709 | 1.4360 | 14.97 | 15.07,<br>15.15 | 57 |

The amides possess an unstable P—N bond, especially in acid solutions. When treated with weak hydrochloric acid solutions the hydrochloride of the corresponding amine is cleaved, while the phosphorus-containing radicals combine into the derivatives of the same pyrophosphonic acids that are formed from the chlorides when treated with water



$$2\,(R)(R'O)P(=O)N(R'')_2 + 2HCl + H_2O \rightarrow (R)(R'O)P(O){-}O{-}P(O)(R)(OR') + 2R''NH \cdot HCl$$

The amides of phosphoric acid behave in a different manner [12].

All of the synthesized amides are biologically active, being cholinesterase inhibitors. The anticholinesterase activity at a molar concentration, causing 50% inhibition, reaches a value as low as $1.5 \cdot 10^{-6}$ (based on cholinesterase serum) for some members. Along with a high anticholinesterase activity the amides show a low toxity. The $LD_{50}$ (intravenous) varies for different members from 2.5 to 1308 mg/kg (for mice). Most of the amides produce myosis, in which connection some of them for a very long time (up to 50 days on cats and human volunteers[*]). Most of the amides are soluble in water. The stability in water solutions is not very great (25-30 days, after which slow decomposition sets in).

## EXPERIMENTAL

*Preparation of the chlorides of alkylalkoxyphosphonic acids.* Into a 2.5-liter three-necked flask, fitted with reflux condenser, stirrer and thermometer, was charged 139 g of ethyl ethylphosphonate and 2 liters of $CCl_4$. A large calcium chloride tube was used to protect the condenser from atmospheric moisture. Dry phosphorus pentachloride (175 g) was added in small portions (1-2 g) with rapid stirring. The addition took 14 hrs, and was done in such a manner that the first $^2/_3$ was added in 7 hrs and the remaining $^1/_3$ in the last 7 hrs. The temperature was maintained at 26-29°. After all of the phosphorus pentachloride had been added the liquid was stirred for another hour. Then the solvent was distilled from the flask at 70-80 mm, and also the formed phosphorus oxychloride and alkyl halide. The residue was distilled at a pressure of 10-12 mm. This method was used to obtain most of the chlorides. Difficulties were encountered in the preparation of substance No. 4 (Table 1) due to the impossibility of obtaining the isopropyl ester of ethylphosphonic acid, either by the Arbuzov method or by the Michaelis method. In the first case the isopropyl ester of isopropylphosphonic acid is obtained as a difficultly separated impurity, due to some "competition" on the part of the formed isopropyliodide. With the Michaelis method the normal product is not formed at all: the main product is the ester salt of the corresponding alkylphosphonic acid. Consequently the desired ester was obtained by the scheme

$$C_2H_5P(OC_3H_7\text{-iso})_2 + O \rightarrow C_2H_5P(O)(OC_3H_7\text{-iso})_2$$

B. p. 88-90° (12 mm), $d_4^{20}$ 0.9764, $n_D^{20}$ 1.4120, $MR_D$ 99.44; calc. 50.01. Found %: P 15.60, 15.65. $C_8H_{19}O_3P$. Calculated %: P 15.46.

The chlorides are liquids with a sharp odor and are readily soluble in most organic solvents.

*Preparation of alkylated amides of alkylalkoxyphosphonic acids.* The amides, with the exception of Nos. 16 and 17 (Table 2), were obtained by the reaction of 1 mole of the chloride with 2 moles of the amine in an inert solvent (usually ether). The reaction temperature was kept at about −15°. After its formation the hydrochloride precipitate was filtered, the solvent was distilled off, and the product was vacuum-distilled.

In the case of ethylenimine the reaction can go in two directions: either with opening of the 3-membered ring (No. 14 in Table 2), or without its opening (No. 13 in Table 2). In the second case the reaction is run with 2 moles of ethylenimine per mole of chloride, and in the first case a 1:1 mole ratio is used.

In most cases the amides are colorless liquids with a pleasant mint or pepper odor. Most of the amides are readily soluble in water, with the exception of compounds Nos. 7, 8, 9 and 15 (Table 2). The amides are radily soluble in many organic solvents.

*Action of water on the chlorides (in the presence of a base).* Into a flask, fitted with condenser, stirrer and thermometer, was charged 47 g (0.3 mole) of the chloride of ethylethoxyphosphonic acid (in benzene solution) and 26.2 g (0.3 mole + 4% excess) of sodium bicarbonate (or pyridine), and then 0.6 mole of water was rapidly added with vigorous stirring. After the stormy reaction, and cooling to room temperature, the precipitate of sodium chloride (or of hydrochloride) was filtered, the benzene was distilled off, and the residue was vacuum-distilled. Yield 6 g (18%).

The obtained product was a colorless liquid with b. p. 139.5-141° (2 mm), $d_4^{20}$ 1.1333, $n_D^{20}$ 1.4280.

Found %: P 24.26, 24.49. $C_8H_{20}O_5P_2$. Calculated %: P 24.09.

*Action of aqueous acid solutions on the amides.* To 100 g of cooled ether, containing 0.5 ml of water and 1.3 g of hydrogen chloride, was added an ether solution (20 ml) of 6 g of the monoethylamide of ethylethoxyphosphonic acid. The next day the precipitate was filtered and weighed 3 g (theory 3 g), m. p. 107-108°. The residue was distilled. The constants were the same as for the substance described above, for which reason the substance was not analyzed. Yield 2.5 g (50%).

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[*] The pharmacological testing was done in the Scientific-Research Chemical-Pharmaceutical Institute (Moscow) by I. M. Sharapov in the laboratory of M. D. Mashovsky, for which the authors express to them their sincere thanks.

## SUMMARY

1. A method was developed which permitted the synthesis of some previously unknown chlorides of alkylalkoxyphosphonic acids..

2. A number of previously unknown alkylated amides of alkylalkoxyphosphonic acids were synthesized and some of the properties of the amides and chlorides were studied.

3. All of the synthesized amides are biologically active, they are cholinesterase inhibitors and produce prolonged myosis.

## LITERATURE CITED

[1] A. Michaelis and J. Ananoff, Ber. 7, 1688 (1874).

[2] A. Michaelis, Lieb. Ann. 293, 193 (1896).

[3] A. Hofmann, Ber. 6, 303 (1873).

[4] F. Güichard, Ber. 32, 1572 (1899).

[5] G. Kosolapoff, Organophosphorus Compounds (New York, 1950), 58.

[6] E. Walsh, T. Beck, and W. Woodstock, J. Am. Chem. Soc. 77, 929 (1955).

[7] K. N. Anisimova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 813.*

[8] K. N. Anisimov, N. E. Kolotova, and A. N. Nesmeyanov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 790.*

[9] A. Ya. Yakubovich and V. A. Ginsburg, J. Gen. Chem. 24, 2250 (1954).*

[10] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Chem. Soc. 61, 217 (1929).

[11] A. I. Razumov, Author's Certificate No. 12249 (1950).

[12] R. Rätz and L. Engelbrecht, Z. allg. anorg. Chem. 272, 326 (1953).

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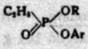
* Original Russian pagination. See C.B. Translation.

# DERIVATIVES OF ALKYLPHOSPHONOUS AND PHOSPHONIC ACIDS

## VII. MIXED ESTERS OF PRIMARY PHOSPHONIC ACIDS*

A. I. Razumov, E. A. Markovich, and A. D. Reshetnikova

**Earlier [1] we had described a method for the preparation of the chlorides of alkylalkoxyphosphonic acids in yields up to 80% of the theoretical [2]. In this paper we describe a second method, which consists in the chlorination of the acid esters of alkylphosphonous acids [3], by analogy with the method for the preparation of the chlorides of dialkylphosphorus acids [4]. In all respects the first of these methods is preferable to the second, and the chlorides, easily obtained in this manner, can be used as starting products for the preparation of various derivatives. In addition, we describe in this paper some mixed esters of primary phosphonic acids, obtained through the indicated chlorides. Very little study has been made of the mixed esters, and there exists only one brief reference in the literature to some esters of methylphosphonic acid [5].**

Mixed Esters of Ethylphosphonic Acid 

| Substance Nos. | Value of | | Boiling point, pressure (in mm) | $d_4^{20}$ | $n_D^{20}$ | Solubility in water | Analysis for phosphorus (in %) | | Yield (in %) |
|---|---|---|---|---|---|---|---|---|---|
| | R | Ar | | | | | calc | found | |
| 1 | $CH_3$ | $C_6H_4NO_2$-p | 159—160° (0.33) | 1.3018 | 1.5294 | 1 : 200 | 5.71 | 5.70,<br>6.02 | 44 |
| 2 | $C_2H_5$ | $C_6H_4NO_2$-p | 163—165 (0.2) | 1.2545 | 1.5242 | 1 : 300 | 5.40 | 5.68,<br>5.70 | 60 |
| 3 | $C_2H_5$ | $C_6H_4NO_2$-o | 140—142 (0.15) | 1.2487 | 1.5115 | 1 : 200 | 5.40 | 5.51,<br>5.57 | 44 |
| 4 | $C_2H_5$ | $C_6H_4NO_2$-o | 145—148 (0.15) | 1.2482 | 1.5110 | 1 : 300 | 5.40 | 5.42,<br>5.56 | 60 |
| 5 | n-$C_3H_7$ | $C_6H_4NO_2$-p | 158—158.5 (0.2) | 1.2231 | 1.5210 | 1 : 700 | 5.14 | 5.46,<br>5.60 | 50 |
| 6 | iso-$C_3H_7$ | $C_6H_4NO_2$-p | 161—164 (0.24) | 1.2286 | 1.5233 | 1 : 600 | 5.14 | 5.44,<br>5.50 | 15 |
| 7 | n-$C_4H_9$ | $C_6H_4NO_2$-p | 181.5—182.5 (0.5) | 1.1968 | 1.5180 | 1 : 1500 | 4.90 | 5.12,<br>5.20 | 57 |
| 8 | iso-$C_4H_9$ | $C_6H_4NO_2$-p | 163.5—164 (0.5) | 1.1971 | 1.5174 | 1 : 1200 | 4.90 | 5.42,<br>5.55 | 22 |
| 9 | $C_2H_5$ | $C_6H_4Cl$-p | 117—118 (0.17) | 1.2122 | 1.5050 | 1 : 800 | 12.48 | 12.40,<br>12.50 | 60 |
| 10 | $C_2H_5$ | $C_6H_4Cl$-o | 106—107 (0.06) | 1.2065 | 1.5045 | 1 : 500 | 12.48 | 12.39,<br>12.54 | 32 |

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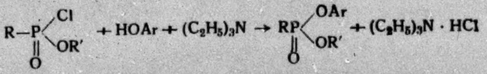
* Presented at the First All-Union Conference on the Chemistry and Use of Organic Phosphorus Compounds (December, 1955, Kazan).

In our opinion, the mixed esters should possess biological activity. The esters were obtained mostly by the scheme–



$$\mathrm{R-\underset{\underset{\displaystyle O}{\|}}{P}\!<\!\begin{smallmatrix}Cl\\OR'\end{smallmatrix} + HOAr + (C_2H_5)_3N \rightarrow R\underset{\underset{\displaystyle O}{\|}}{P}\!<\!\begin{smallmatrix}OAr\\OR'\end{smallmatrix} + (C_2H_5)_3N\cdot HCl}$$

All of the esters (see table) are either colorless (in the case of the chlorophenyl radical) or yellow-colored (in the case of the nitrophenyl radical) liquids. The esters are quite readily soluble in water and in aqueous solutions, and are stable both when stored for a long time (at least up to 3 yrs) and when heated (during sterilization). They are rapidly hydrolyzed in alkaline solutions. All of the mixed esters are strong cholinesterase inhibitors and produce myosis.* The ethyl p-nitrophenyl ester of ethylphosphonic acid (No. 2) is the most biologically active compound: the minimum concentration, producing myosis, is a 1 : 200,000 solution, and the anticholinesterase activity is equal to $2 \cdot 10^{-9}$ (based on the actual cholinesterase, by the Warburg method [6]). This ester, known in medical practice under the name of "Armine," is used for the treatment of glaucoma and some other maladies [7]. In its medicinal properties it is superior to the preparation of Schrader [8], known in medicine under the name of "Mintacol" (phosphacol).

## EXPERIMENTAL**

Preparation of the chloride of ethyl-ethoxyphosphonic acid. The chloride was obtained from the acid ethyl ester of ethylphosphonous acid. The constants of the ester differ somewhat from the literature data [3]: b. p. 77.5° at 15 mm, $d_4^{20}$ 1.0779, $n_D^{20}$ 1.4262. For reaction we took 13.4 g of the acid ester. The ester was cooled in a flask to −15°, and then a stream of dry chlorine was passed through it until a very faint yellow color was obtained. On termination of chlorine passage the excess chlorine was removed with a nitrogen stream in vacuo at room temperature, and then the product was distilled. We obtained 6 g of product (36%). The chloride had the same constants as that obtained by a different method [1].

Preparation of ethyl p-nitrophenyl ethylphosphonate. Into a 3-liter three-necked flask, fitted with reflux condenser, thermometer and dropping funnel, was charged 181 g of p-nitrophenol and 1500 ml of dry ether. After the phenol had dissolved, 204.5 g of ethylethoxyphosphonic chloride was added. Then the flask was placed in a bath containing cold water, and the contents stirred for 40-45 min. After this 132 g of triethylamine, diluted with three volumes of dry ether, was added slowly. When all of the amine had been added the contents of the flask were heated for 30-40 min at solvent boil. After cooling the mixture the hydrochloride was filtered, while the mixed ester was distilled twice in a high vacuum (pressure not exceeding 0.2 mm, since the product shows a tendency to decompose at higher pressures). Yield 206 g (61%).

Most of the other mixed esters were prepared in a similar manner. Only in some cases were the anhydrous phenolates used. The first method is to be preferred.

## SUMMARY

1. Some previously unknown mixed esters of ethylphosphonic acid were synthesized.

2. All of the synthesized mixed esters show biological activity as cholinesterase inhibitors and as powerful myotics.

## LITERATURE CITED

[1] A. I. Razumov, O. A. Mukhacheva, and E. A. Markovich, J. Gen. Chem. 27, 2389 (1957).***

[2] A. I. Razumov, Author's Certificate No. 12249 (1950).

[3] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 956.***

[4] H. McCombie, B. Saunders, and G. Stacey, J. Chem. Soc. 1945, 381.

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* The pharmacological properties of the mixed esters of primary phosphonic acids were studied by M. A. Aluf and her co-workers (Kazan Medical Institute), for which the authors express to them their sincere thanks.

** The experimental work was done in 1949-1952.

*** Original Russian pagination. See C.B. Translation.

[5] G. Kosolapoff, Organophosphorus Compounds (New York, 1950), 149.

[6] M. A. Aluf, J. Pharmacology and Toxicology (USSR) No. 2, 21 (1955).

[7] A. I. Razumov and M. A. Aluf, Author's Certificate No. 102461 (1955).

[8] G. Schrader, Z. ang. Chem. 62, 471 (1950).

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# ISOMERIZATION OF MONOOLEFINIC HYDROCARBONS UNDER THE CONDITIONS OF CATALYTIC HYDROGENATION IN A LIQUID PHASE

I. V. Gostunskaya, N. B. Dobroserdova, and B. A. Kazansky

In his well-known studies on the catalytic hydrogenation of dienes in the presence of platinum black S. V. Lebedev [1, 2] set himself the goal of establishing the relationship between the structure of dienes and the manner in which the first molecule of hydrogen added to them. It proved that the addition went in all of the possible directions (in positions 1, 2; 3, 4; and 1,4) with an ill-defined selectivity; usually the reaction products were also found to contain the unreacted diene and an equivalent amount of the paraffin – the addition product of two molecules of hydrogen to the diene.

TABLE 1

| Dienes | Composition of mixture of monoolefins in % | | Catalysts | | |
|---|---|---|---|---|---|
| | manner in which 1 mole of $H_2$ adds | monoolefins | Pt | Pd | Ni |
| Isoprene | 1,4 | 2-Methyl-2-butene | 31 | 43 | 42 |
| | 1,2 + 3,4 | 2-Methyl-1-butene + 3-methyl-1-butene | 69 | 57 | 58 |
| Diisocrotyl | 1,4 | 2,5-Dimethyl-3-hexene | 17 | 7 | 9 |
| | 1,2 + 3,4 | 2,5-Dimethyl-2-hexene | 83 | 93 | 91 |

The studies of S. V. Lebedev were extended and made more complete later by other investigators [3-6]; under the same conditions hydrogen was added to diisocrotyl, isoprene, diisopropenyl and 3-methyl-2-ethyl-1,3-pentadiene in the presence of not only platinum, but also palladium black and skeletal nickel, and a more detailed investigation of the reaction products was made. Here it was found that a somewhat greater selectivity in the addition of the first molecule of hydrogen is observed in the presence of palladium or nickel than in the presence of platinum. Thus, unreacted diene and completely hydrogenated paraffin are found to a considerably smaller extent in the reaction products, while the amount of hydrogen, adding to the diene in the 1,4 position, shows a greater variation as a function of the structure of the diene being hydrogenated, which can be seen from the data given in Table 1.

For all of the investigated hydrocarbons, in the presence of all three catalysts, the addition of hydrogen in the 1,2 and 3,4 positions (as a sum) predominates over the addition in the 1,4 position. However, the composition of the monoolefins, obtained as a result of the addition of one molecule of hydrogen to isoprene and diisocrotyl in the presence of palladium and nickel, is closer to the composition of the equilibrium mixture of olefins than obtains in the hydrogenation over platinum. Actually, the experimental and calculation data show that for temperatures, close to those at which the described experiments were run, the predominant component in the equilibrium mixture of methylbutenes is the 2-methylbutene with a central position of the double bond [7], while in the equilibrium mixture of 2,5-dimethylhexenes the predominant component is 2,5-dimethyl-2-hexene [8], in which the double bond is located in the 1,2 (or 3,4) position of the conjugated system.

It is possible to assume that the composition of the monoolefins, formed as the result of the addition of one molecule of hydrogen to dienes of variable structure, depends not only on the structure of the starting dienes, as was assumed by S. V. Lebedev, but also on the secondary reaction of isomerization of the olefins with a shift of the double bond, progressing in the presence of various catalysts at various rates.

Statements exist in the literature that such a shift is possible in the presence of metallic hydrogenation catalysts. Thus, as early as 1929 Zelinsy and Levina [9] observed that 3,7-dimethyl-1-octane in the presence of palladinized asbestos at 200° isomerizes with a shift of the double bond to the middle of the carbon chain. Later, Twigg [10-11] observed a shift of the double bond when 1-butene was brought in contact with a nickel wire in a hydrogen atmosphere at 65° and at 133°. Young and co-workers [12], in studying the hydrogenation of butadiene with various catalysts at hydrogen pressures of 1-2 atmospheres and room temperature in ethyl alcohol medium, revealed that in the presence of palladium, deposited on barium sulfate, the composition of the partially hydrogenated products was close to the composition of the thermodynamic equilibrium mixture of butenes. The migration of the double bond in butenes was confirmed by them by means of special experiments in which 1-butene and 2-butene were subjected to partial hydrogenation in the presence of the same catalysts. Kazansky, Lukina, Malyshev and others [13] observed the isomerization of 2-methyl-1-pentene and 2-methyl-2-pentene in an equilibrium mixture of these olefins of identical composition in the partial hydrogenation of each of these hydrocarbons in alcohol medium at room temperature in the presence of palladium black. Kazansky and Popova [3] tried to isomerize 2,5-dimethyl-2-hexene into 2,5-dimethyl-3-hexene by subjecting it to partial hydrogenation at room temperature in the presence of either platinum black or skeletal nickel; however, they failed to observe any appreciable isomerization. This can be explained by the fact that under the conditions used by these authors, the equilibrium concentration of 2,5-dimethyl-3-hexene should have been quite small, as follows from the experiments made later on the isomerization of the 2,5-dimethylhexenes in the presence of calcium amide [8].

The purpose of the present study was to determine to what degree in the hydrogenation of dienes in the presence of the three enumerated catalysts it is possible for the double bond in the monoolefins, formed as intermediate products, to shift. For this 2-methyl-1-butene and 3-methyl-1-butene – the intermediate products in the partial hydrogenation of isoprene – were shaken in 95% alcohol medium at room temperature with such amounts of either platinum or palladium black or skeletal nickel as were used in the earlier described studies on the hydrogenation of dienes [3-6], in which connection from 0.15 to 0.30 mole of hydrogen was introduced into the hydrogenation vessel. The same technique in the presence of palladium black was also used in the case of 2,5-dimethyl-3-hexene, which is formed when 1 mole of $H_2$ is added to diisocrotyl.

As a result of the performed experiments it was found that in all cases when platinum black was used only hydrogen addition occurs, i. e., a shift of the double bond failed to occur. In the presence of palladium black, together with hydrogen addition, there was also isomerization: 2-methyl-1-butene was almost completely isomerized into 2-methyl-2-butene; 3-methyl-1-butene was ~ 30% converted into the same hydrocarbon; and 2,5-dimethyl-3-hexene was almost completely converted into 2,5-dimethyl-2-hexene. A shift of the double bond also occurred in the presence of nickel, but to a much lesser degree than in the presence of palladium black. As a result it is possible to assume that in the presence of palladium black the addition of the first molecule of hydrogen to dienes, according to S. V. Lebedev, should not be accompanied by any secondary isomerization phenomena. In the presence of palladium, and to a lesser degree in the presence of nickel, it is possible for the isomerization reaction to reflect on the composition of the final products of the partial hydrogenation of dienes. In the presence of palladium the isomerization rate for the hydrocarbons mentioned in the present study is greater than their hydrogenation rate, and in the presence of nickel the reverse is true.

Such a sharply expressed difference in the ability of platinum and palladium to catalyze a shift of the double bond under the indicated conditions cannot as yet be satisfactorily explained due to the absence of reliable data, which would characterize the state of the hydrogen on a platinum or palladium black surface, and also the absence of reliable data on the different ratios that exist between the amount of hydrogen adsorbed on the surface of these metals and that dissolved in them. It is obvious that a difference in these ratios can exert a variable effect on the behavior of the mentioned catalysts in the reaction for the isomerization of olefins; it is necessary to assume that a further accumulation of experimental data will permit throwing some light on this subject.

## EXPERIMENTAL

**Starting monoolefins.** 2-Methyl-1-butene and 3-methyl-1-butene were prepared by the dehydration of isoamyl alcohol (passage of the vapors over aluminum oxide at 400° and a space velocity of 1); the dehydration products were distilled through a 70-theoretical plate column. 2,5-Dimethyl-3-hexene was synthesized by the method of [14], i. e., by the reaction of $CH_3MgBr$ with 2,5-dichloro-3-hexene. The hydrocarbon was distilled through a 40-theoretical plate column. The properties of the olefins are given in Table 2.

TABLE 2

| Name of olefin | Boiling point (760 mm) | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ |  | Literature data |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | found | calc. | Boiling point (760 mm) | $n_D^{20}$ | $d_4^{20}$ | source |
| 3-Methyl-1-butene | 20.2 | 1.3672 (15°) | 0.6328 (15°) | 24.90 | 24.82 | 20.06 | 1.3675 (15°) | 0.6325 (15°) | [15] |
| 2-Methyl-1-butene | 31.2 | 1.3777 | 0.6500 | 24.86 | 24.82 | 31.16 | 1.3778 | 0.6504 | [15] |
| 2,5-Dimethyl-3-hexene | 99.7—99.9 | 1.4040 | 0.7015 | 39.11 | 38.67 | 103—103.5<br>102—102.1 | 1.4100<br>1.4030 | 0.7122<br>0.7124 | [14,16]<br>[17] |

TABLE 3

| Expt. No. | Catalyst | Amount (in mole %) |  | Total composition of reaction mixture (in wt. %) |  |  | Comp. of reaction mixture calc. on basis of the monoolefins (in wt. %) |  |
|---|---|---|---|---|---|---|---|---|
|  |  | catalyst | $H_2$ | 2-methyl -1- butene | 2-methyl -2- butene | 2-methylbutane | 2-methyl -1- butene | 2-methyl -2- butene |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 1 | Pd | 1.0 | 13.9 | 7.1 | 79.6 | 13.3 | 8.2 | 91.8 |
| 2 | Pt | 1.0 | 14.0 | 90.6 | — | 9.4 * | 100 | 0 |
| 3 | Ni | 1.0 | 14.2 | 88.0 | — | 12.0 | 100 | 0 |
| 4 | Ni | 10.0 | 13.9 | 77.2 | 8.9 | 13.9 | 89.7 | 10.3 |
| 5 | Ni | 1.0 | 27.4 | 73.4 | 3.5 | 23.1 | 95.5 | 4.5 |

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* The low content of 2-methylbutane in the reaction products is explained by the losses incurred during distillation.

TABLE 4

| Expt. No. | Catalyst | Amount (in mole %) |  | Total composition of the reaction mixture ( in wt. %) |  |  | Comp. of reaction mixture calc. on the basis of the monoolefins (in wt. %) |  |
|---|---|---|---|---|---|---|---|---|
|  |  | catalyst | $H_2$ | 3-methyl -1- butene | 2-methyl -2- butene | 2-methylbutane | 3-methyl -1- butene | 2-methyl -2- butene |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 6 | Pd | 1.0 | 14.3 | 57.2 | 27.2 | 15.6 | 67.8 | 32.2 |
| 7 | Pt | 1.0 | 14.0 | 85.5 | — | 14.5 | 100.0 | 0 |
| 8 | Ni | 1.0 | 27.8 | 71.5 | 1.9 | 26.6 | 97.4 | 2.6 |

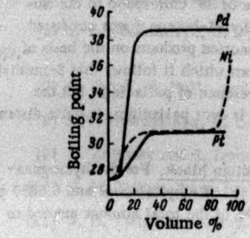

Fig. 1. Distillation curves for the products of the partial hydrogenation of 2-methyl-1-butene in the presence of palladium, platinum or nickel.

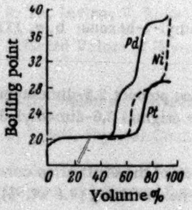

Fig. 2. Distillation curves for the products of the partial hydrogenation of 3-methyl-1-butene in the presence of palladium, platinum or nickel.

Operational technique and study of the reaction products. The hydrogenations were run at room temperature and atmospheric pressure in 95% ethyl alcohol medium (250 ml). The palladium and platinum blacks were taken in amounts of 1-1.5 mole% on the weight of the olefin, while the nickel was taken in amounts of 1 and 10%. The amount of hydrogen added was approximately 14 to 28% of that needed to completely hydrogenate the taken weight of olefin. The reaction products were studied by the method described in previous papers [3-5].

Partial hydrogenation of 2-methyl-1-butene. The amount of olefin taken for each experiment was 35 g (0.5 mole). The experimental conditions and composition of the reaction products are given in Table 3.

The distillation curves for expt. Nos. 1, 2, and 5 are shown in Fig. 1.

The portions of the distillation curves with a temperature of about 28° correspond to the saturated hydrocarbon – isopentane (b. p. 27.8°), the portions of the curves at 31° correspond to the original 2-methyl-1-butene, and those at a temperature of 38° – to the isomerization product 2-methyl-2-butene (b. p. 38.6°). The third possible amylene – 3-methyl-1-butene – was not found in the reaction products.

Columns 8 and 9 in Table 3 give the data on the amount of isomeric olefins in the reaction mixture calculated on the basis of 100% olefins, without taking into account the amount of isopentane formed as the result of the addition of hydrogen to the olefin.

Calculation of the composition of the thermodynamic equilibrium mixture of isoamylenes for a temperature of 25°, made on the basis of the isobaric potential values given in the tables [18], gives the following results: 2-methyl-2-butene 92%, 2-methyl-1-butene 7.8%, and 3-methyl-1-butene 0.2%.

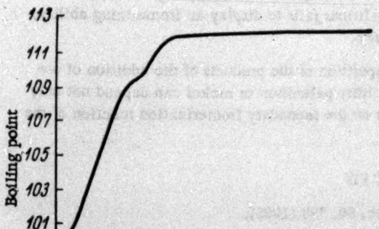

Fig. 3. Distillation curve for the products of the partial hydrogenation of 2,5-dimethyl-3-hexene in the presence of palladium.

A comparison of the results of the partial hydrogenation of 2-methyl-1-butene in the presence of either Pd or Ni with the composition of the equilibrium mixture of isoamylenes reveals that in the case of palladium the isomerization proceeds quantitatively up to the equilibrium concentrations of the isoamylenes. The isomerizing action of nickel, studied in expt. Nos. 3-5, becomes noticeable only when the amount of catalyst taken is increased up to 10% (Expt. 4), or when the amount of added hydrogen is increased (by increasing the contact time).

Partial hydrogenation of 3-methyl-1-butene. The amount of monoolefin taken for each hydrogenation experiment was 35 g (0.5 mole). The conditions and results of the experiments are presented in Table 4. The distillation curves are shown in Fig. 2.

The portions of the distillation curves with a temperature of 20° correspond to the original 3-methyl-1-butene, the portions with a temperature of 28° correspond to the hydrogenation product — isopentane — and those with a temperature of 38° correspond to the isomerization product — 2-methyl-2-butene. The third possible amylene — 2-methyl-1-butene — was not found in the partial hydrogenation products. Calculation of the composition of the reaction products on the basis of 100% monoolefins gives the results presented in columns 8 and 9 of Table 4, from which it follows that 3-methyl-1-butene, the same as 2-methyl-1-butene, is most rapidly isomerized in the presence of palladium, but the composition of the obtained mixture of amylenes, even when the isomerization is over palladium, is quite distant from the composition of the thermodynamic equilibrium mixture of amylenes.

Partial hydrogenation of 2,5-dimethyl-3-hexene in the presence of palladium black. For the hydrogenation we took a solution of 20.5 g (0.17 mole) of 2,5-dimethyl-3-hexene in 250 ml of ethyl alcohol and 0.5350 g (0.0027 g-atoms) of palladium black. The amount of hydrogen added was 15.7% of the total amount needed to completely hydrogenate the taken weight of olefin.

The distillation curve for the hydrogenation products is shown in Fig. 3. The straight portion of the distillation curve with a temperature of about 112° corresponds to the isomerization product, 2,5-dimethyl-2-hexene, possibly containing some 2,5-dimethyl-1-hexene, the properties of which lie quite close to those of 2,5-dimethyl-2-hexene.

2,5-Dimethyl-2-hexene: b. p. 112.2°, $n_D^{20}$ 1.4120, $d_4^{20}$ 0.7182; 2,5-dimethyl-1-hexene: b. p. 111.6°, $n_D^{20}$ 1.4105, $d_4^{20}$ 0.7172.

The inflection on the curve at about 109° corresponds to the hydrogenation product 2,5-dimethylhexane (b. p. 109.1°), while the inflection at about 100° testifies to the presence of the original 2,5-dimethyl-3-hexene in the mixture.

Calculation of the composition of the reaction products, made on the basis of the distillation curve and analysis of the obtained fractions, gives the following results: 2,5-dimethyl-3-hexene 1.6 g (9.5 wt. %), 2,5-dimethyl-2-hexene 11.9 g (70.9 wt. %), and 2,5-dimethylhexane 3.3 g (19.6 wt. %).

The unsaturated portion of the catalyzate contains 11.3% of original 2,5-dimethyl-3-hexene and 88.7% of the isomerization product — 2,5-dimethyl-2-hexene.

## SUMMARY

1. The isomerization of 2-methyl-1-butene and 3-methyl-1-butene in the presence of platinum black, palladium black and Raney nickel, and also the isomerization of 2,5-dimethyl-3-hexene in the presence of palladium black, was studied under the conditions of partial hydrogenation of the olefins at room temperature and atmospheric pressure in ethyl alcohol medium.

2. It was shown that in the presence of palladium all of the investigated olefins undergo isomerization with a shift of the double bonds. Platinum under the studied conditions fails to display an isomerizing ability, while nickel causes the double bond to shift only to a slight degree.

3. The observations made testify to the fact that the composition of the products of the addition of one molecule of hydrogen to diene hydrocarbons in the presence of either palladium or nickel can depend not only on the manner in which the hydrogen adds to the diene, but also on the secondary isomerization reaction of the formed monoolefins.

## LITERATURE CITED

[1] S. V. Lebedev and A. I. Yakubchik, J. Russ. Chem. Soc. 60, 793 (1928).

[2] S. V. Lebedev and A. I. Yakubchik, J. Russ. Chem. Soc. 59, 981 (1927).

[3] B. A. Kazansky and N. I. Popova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1952, 422;* Scientific Memoirs Moscow State Univ. 151, 69 (1951).

[4] B. A. Kazansky, I. V. Gostunskaya, and A. M. Granat, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 670.*

---

* Original Russian pagination. See C.B. Translation.

[5] I. V. Gostunskaya, E. A. Krasnyanskaya, and B. A. Kazansky, J. Gen. Chem. 25, 1448 (1955).*

[6] I. V. Gostunskaya, G. V. Loza and B. A. Kazansky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 863.*

[7] G. Egloff, G. Hulla, and V. I. Komarewsky, Isomerization of Pure Hydrocarbons (New York, 1942), 61.

[8] I. V. Gostunskaya, N. I. Tyunkina, and B. A. Kazansky, Proc. Acad. Sci. USSR 108, 473 (1956).*

[9] N. Zelinsky and R. Levina, Ber. 62, 1861 (1929); N. D. Zelinsky, Selected Works (1955), Vol. III, 389.* *

[10] G. H. Twigg, Trans. Far. Soc. 35, 934 (1939).

[11] G. H. Twigg, Proc. Roy. Soc. 178A, 106 (1941).

[12] W. G. Young, R. L. Meier, J. Vinograd, H. Bollinger, L. Kaplan, and S. Linden, J. Am. Chem. Soc. 69, 2046 (1947).

[13] B. A. Kazansky, M. Yu. Lukina, A. I. Malyshev, V. T. Aleksanyan, and Kh. E. Sterin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 36.*

[14] R. Ya. Levina, V. R. Skvarchenko, E. G. Treshchova, and V. M. Tatevsky, J. Gen. Chem. 20, 49 (1950).*

[15] Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds (1953).

[16] R. D. Obolentsev, Physical Constants of Hydrocarbons, Liquid Fuels and Oils (1953).* *

[17] G. Egloff, Physical Constants of Hydrocarbons (1939).

[18] A. A. Vvedensky, Thermodynamics Calculations of Processes of the Fuel Industry(State Sci.-Tech. Press of Petroleum and Mineral Fuel Literature, 1949).* *

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* * Original Russian pagination. See C.B. Translation.

* * In Russian.

# THE INVESTIGATION OF CONJUGATED SYSTEMS

## LXXXI. THE ORDER OF BROMINE ADDITION TO DIALKYLVINYLETHYNYLCARBINOLS

A. A. Petrov and K. B. Rall

As the result of investigations by one of us together with Yu. I. Porfiryeva, specific rules were established for the addition reactions of vinylethynyl hydrocarbons. It was shown that bromine adds on to the double bond of vinylalkylacetylenes, while alkenylacetylenes give mainly allene dibromides (1,4-addition) [1, 2]. With hydrogen bromide, vinylalkylacetylenes form allene hydrobromides, but alkenylacetylenes give 1,3-diene hydrobromides (addition to the triple bond) [3]. Hydrogen adds on to the triple bond in all cases [4]. Hydrocarbons with isolated multiple bonds add bromine to double bonds and hydrogen bromide to triple bonds [5].

It was of interest to investigate the rules of addition for derivatives of vinylacetylene hydrocarbons. With this object in view we have investigated the addition of bromine to dialkylvinylethynylcarbinols.

Dialkylvinylethynylcarbinols have recently been investigated in detail, particularly by the school of I. N. Nazarov [6]; but for their simple addition reactions (with halogens, hydrogen halides, etc.) only a little data is available.

Hydrogen (by catalytic reduction or nascent) adds exlusively to the triple bond [6 - 8]. The action of a hydrogen halide is first to form the dialkylvinylethynylmethyl halide which then adds on a molecule of hydrogen halide to give compounds of the type — $R_2CX-CH=CX-CH=CH_2$ and $R_2C=CH-CX=CH-CH_2X$ [9, 10]. Alkyl hypoiodites, on the other hand, add preferentially to the double bond [11]. Dienes synthetized with the aid of dialkylvinylethynylcarbinols (in the capacity of dienophils) add exclusively to the double bond [6]. The addition of nucleophilic substances to the triple bond is a trivial fact.

As subject for investigation we selected the two alcohols — dimethylvinylethynylcarbinol and diisopropylvinylethynylcarbinol.

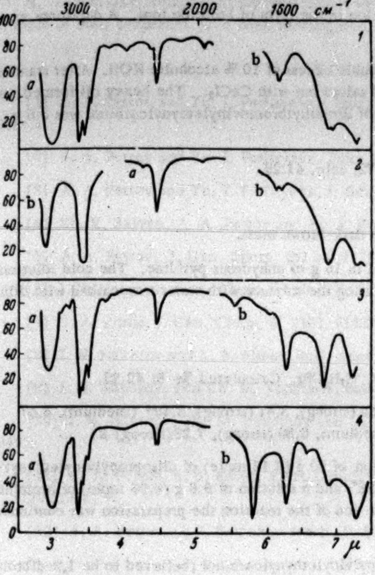
By the bromination of these alcohols there was the possibility of forming three isomeric dibromides — an allene (by 1,4-addition), an acetylene (by addition to the double bond) and a 1,3-diene (by addition to the triple bond).

In practice the bromination of these carbinols gave compounds with fairly narrow boiling ranges, which readily lost one molecule of hydrogen bromide under the influence of cold alcoholic alkali. These properties showed at least that the compounds were mainly dibromides with mobile bromine atoms, acetylene or allene.

The infrared spectra of both the dibromides (Fig. 1, curves 1 and 2) showed only slight absorption in the region of 5.09 $\mu$, so that the presence of any significant amount of allene dibromide could be excluded. At the same time the spectra showed quite strong bands at about 4.4 $\mu$ which were characteristic of acetylene compounds [12]. The bands characteristic of 1,3-dienes at 6.10-6.25 $\mu$ were of low intensity.

Thus the spectral data left no doubt that we were dealing with acetylene dibromides containing small amounts of 1,3-diene and very small amounts of allene dibromides. It followed that the dialkylvinylethynylcarbinols added bromine to the double bond like the structurally related hydrocarbons — the vinylalkylacetylenes.

We further investigated the products obtained by the action of alcoholic alkali on the dibromides of the dialkylvinylethynylcarbinols. The triple bond between the carbon atoms linked to bromine and the ternary hydroxyl group could not become part of a five- or six-membered ring, so that the elimination of hydrogen bromide would not affect the alcoholic hydroxyl group. The result of dehalogenation was to give only the very unstable bromovinylethynyl alcohol — $R_2C(OH)-C\equiv C-CBr=CH_2$.



Infrared Spectra.
1) Dibromide of dimethylvinylethynylcarbinol;
2) dibromide of diisopropylvinylethynylcarbinol;
3) product of the reaction of the dibromide of diisopropylvinylethynylcarbinol with alcoholic alkali; 4) acetylation product of dimethylbromovinylethynylcarbinol.
Curves "a" were obtained with a LiF prism, curves "b" with a NaCl prism. The cell thickness was 0.1 mm.

The infrared spectra of these compounds were used to check their proposed structures. The spectra showed strong absorption bands corresponding to hydroxyl (2.9 μ) and to double (6.26 μ) and triple (4.44 μ) bonds (curve 3 of Fig. 1 is for diisopropylbromovinylethynylcarbinol).

Experiments on the conversion of these alcohols into acetates (by the action of acetyl chloride in pyridine) showed that acetylation occurred with great difficulty. In the case of dimethylbromovinylethynylcarbinol the product was a mixture of the acetate (about 56 %) with the original alcohol. The infrared spectrum of this mixture (Fig. 1, curve 4) showed bands corresponding to hydroxyl (2.98 μ), carbonyl (5.78 μ) and to the ethylenic (6.26 μ) and acetylenic (two at 4.43 and 4.45 μ) bonds. In the case of diisopropylbromovinylethynylcarbinol acetylation was not achieved; the original carbinol was recovered unchanged. This peculiarity in the behavior of the alcohols is clearly the result of steric difficulties.

## EXPERIMENTAL

The technical grade of dimethylvinylethynylcarbinol was used. It was redistilled in vacuo. The b. p. 52° (10 mm) and $n_D^{20}$ 1.4780 agreed with the data in the literature [6].

Diisopropylvinylethynylcarbinol was obtained as follows. An ethereal solution of vinylacetylene (20 % excess) was added in small portions, with cooling, to a solution of a Grignard reagent prepared from ethyl bromide. After the evolution of ethane had finished, the solution was treated with the calculated quantity of isobutyrone. The preparation was then continued in the normal way. The yield of diisopropylvinylethynylcarbinol was 66 %.

B. p. 76-77° (8 mm), 82-83° (10 mm), $d_4^{20}$ 0.8832, $n_D^{20}$ 1.4790, molecular refraction (MR) 53.38, calc. 51.99.

Found %: C 79.31, H 11.08. $C_{11}H_{18}O$. Calcualted %: C 79.54, H 10.91.

Bromination of dimethylvinylethynylcarbinol. A solution of 65 g (0.6 mole) of dimethylvinylethynylcarbinol in 200 ml of chloroform was maintained at minus 25-28°, and 48 g (0.3 mole) of bromine in 50 ml of chloroform was added with vigorous stirring over a period of 1.5 hours. At the end of the reaction the chloroform was distilled off slowly on a water bath. The pressure was then reduced to 10 mm, and unreacted carbinol (37.2 g) was distilled off. The reaction product was redistilled at 4 mm.

The dibromide of dimethylvinylethynylcarbinol (mainly 1,2-dibromo-5-methyl-3-hexyn-5-ol) was obtained in 82 % yield (based on the bromine).

B. p. 99-101.5° (4 mm), $d_4^{20}$ 1.7273, $n_D^{20}$ 1.5519, MR 49.92, calc. 49.58.

Found %: Br 59.10. $C_7H_{10}OBr_2$. Calculated %: Br 59.22

Infrared spectrum — 2.95 (strong), 3.34 (strong), 3.41 (strong), 3.49* (strong), 4.01 (weak), 4.34 (weak),

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* Shoulder.

4.41 (medium), 5.08 (very weak), 6.14 (medium), 6.20 (medium), 6.87 (strong), 6.92 (strong), 7.26 (strong) μ.

When 2.3420 g of the dibromide was treated in the cold with a two-fold excess of 10% alcoholic KOH, 0.74 g of bromine, 53.4 % of the total weight, appeared in the solution in the form of bromide ions. A duplicate experiment gave 53.7 %.

The dibromide (20.2 g) was treated in the cold with a double excess of 10 % alcoholic KOH. After standing for 2.5 hours the mixture was diluted with water, acidified and salted out with $CaCl_2$. The heavy oil formed was separated, dried over $CaCl_2$ and distilled in vacuo. The yield of dimethylbromovinylethynylcarbinol was 5.6 g (40 %).

B. p. 72-73.5° (5 mm), $d_4^{20}$ 1.3214, $n_D^{20}$ 1.5232, MR 43.72, calc. 41.29.

Found %: Br 40.93. $C_7H_9OBr$. Calculated %: Br 42.27.

The material visibly darkened and soon turned to a thick dark-brown mass.

Dimethylbromovinylethynylcarbinol (8.8 g) was dissolved in 16 g of anhydrous pyridine. The cold solution was treated with 5 g of acetyl chloride. The oil formed on diluting the mixture with water was washed with dilute sulfuric acid, dried and distilled in vacuo. Yield 5.7 g.

B. p. 78-80° (5 mm), $d_4^{20}$ 1.2926, $n_D^{20}$ 1.5122.

Found %: Br 37.94. $C_9H_{11}O_2Br$. Calculated %: Br 34.58. $C_7H_9OBr$. Calculated %: Br 42.27.

Infrared spectrum — 2.98 (strong), 3.21* (medium), 3.35 (strong), 3.41 (strong), 3.49* (medium), 4.43 (medium), 4.45 (medium), 5.78 (strong), 6.26 (strong), 6.57 (medium), 6.89 (strong), 7.28(strong) μ.

Bromination of diisopropylvinylethynylcarbinol. A solution of 20 g (0.12 mole) of diisopropylvinylethynylcarbinol in 100 ml of chloroform was maintained at minus 25-28°, and a solution of 9.6 g (0.06 mole) of bromine in 50 ml of chloroform was added with vigorous stirring. At the end of the reaction the preparation was continued as described above.

The yield was 15.6 g (80 %) of the dibromide of diisopropylvinylethynylcarbinol (believed to be 1,2-dibromo-6-methyl-5'-metho-5-ethyl-3-heptyn-5-ol).

B.p. 134-136° (4 mm), $d_4^{20}$ 1.4529, $n_D^{20}$ 1.5295, MR 69.29, calc. 68.05.

Found %: Br 49.68, 49.40. $C_{11}H_{18}OBr_2$. Calculated %: Br 49.03.

Infrared spectrum — 2.98 (strong), 3.40 (strong), 4.42 (medium), 6.08 (weak), 6.22 (weak), 6.81 (strong), 7.26 (strong) μ.

It should be noted that dibromides were obtained with a wider boiling range in individual experiments, which was explained as the result of isomerization during the process of distillation.

When a small quantity of the substance was treated in the cold with alcoholic alkali about 50 % of the bromine always went into solution.

A twofold excess of 10 % alcoholic KOH was added to 17 g of the dibromide in the cold. The resulting mixture was treated as described above to obtain 7.9 g (64 %) of diisopropylbromovinylethynylcarbinol.

B. p. 99-100.5° (5 mm), $d_4^{20}$ 1.1980, $n_D^{20}$ 1.5145, MR 61.65, calc. 59.82.

Found %: Br 32.58. $C_{11}H_{17}OBr$. Calculated %: Br 32.60.

Infrared spectrum — 2.90 (strong), 3.21 (weak), 3.36 (strong), 3.41* (strong), 3.49 (strong), 3.67 (weak), 3.83 (weak), 4.18 (weak), 4.44 (medium), 5.51 (weak), 6.26 (strong), 6.81 (strong), 7.22 (strong) μ.

## SUMMARY

1. The order of the addition of bromine to dimethyl- and diisopropylvinylethynylcarbinols has been investigated.

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* Shoulder.

2. It has been shown that the predominating product in both cases was the acetylene dibromide; bromine added mainly to the double bond.

3. Two dialkylbromovinylethynylcarbinols were obtained by the action of alcoholic alkali on the dibromides, and some of their properties have been investigated.

## LITERATURE CITED

[1] A. A. Petrov and Yu. I. Porfiryeva, Proc. Acad. Sci. USSR, 89, 873 (1953); J. Gen. Chem. 23, 1867 (1953).*

[2] A. A. Petrov and Yu. I. Porfiryeva. Proc. Acad. Sci. USSR, 111, 839 (1956).*

[3] A. A. Petrov and Yu, I. Porfiryeva, J. Gen. Chem. 27, 94 (1957).*

[4] Kh. V. Balyan, A. A. Petrov and Yu. I. Porfiryeva, J. Gen. Chem. 26, 1926 (1956)*; 27, 365 (1957).*

[5] A. A. Petrov, J. Gen. Chem. 27, 3319 (1956).*

[6] I. N. Nazarov, Prog. Chem. 14, 3 (1945).

[7] S. A. Zonis, J. Gen. Chem. 9, 2191, (1939).

[8] I. N. Nazarov and L. B. Fisher, Bull. Acad. Sci. USSR, Div. Chem. Sci. 71 (1944).

[9] I. N. Nazarov, and Ya. M. Yanbikov, Bull Acad. Sci. USSR, Div. Chem. Sci. 66 (1943).

[10] I. N. Nazarov, Ya M. Yanbikov and M. V. Kuvarzina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 135 (1942).

[11] A. A. Petrov, E. S. Bravo, V. V. Davidovich, O. S. Dyatkova and G. V. Kuznetsova. J. Gen. Chem. 23, 1120 (1953).*

[12] A. A. Petrov, G. I. Semenov and N. P. Sopov, J. Gen. Chem. 27, 928 (1957).*

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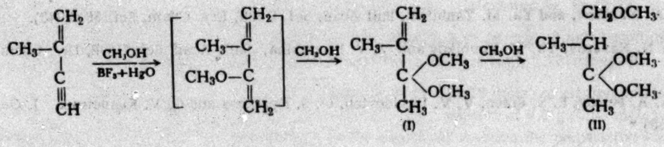
# HOMOLOGS OF MONOVINYLACETYLENE

## VI. THE ADDITION OF METHYL ALCOHOL TO ISOPROPENYLACETYLENE

I. A. Favorskaya and N. N. Kopylov-Shakhmatov

The addition of methyl alcohol to isopropenylacetylene at room temperature led to the formation of two products, the dimethylketal of 2-methyl-1-buten-3-one (I) and the dimethylketal of 1-methoxy-2-methyl-3-butanone (II).



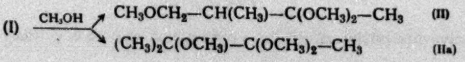
If the addition was carried out at a higher temperature (40° ), the only reaction product obtained was product (II). The results of individual experiments on the addition of the alcohol are given in Table 1.

TABLE 1

| Expt. No. | Amounts of reagents (in moles) | | Duration of reaction (in hours) | Temperature | Yield of product (%) | |
|---|---|---|---|---|---|---|
| | hydrocarbon | alcohol | | | (I) | (II) |
| 1 | 0.5 | 2.0 | 9 | 30° | 21.5 | 24.7 |
| 2 | 0.68 | 2.45 | 20 | 40 | — | 40 |
| 3 | 0.72 | 2.75 | 17 | 40 | — | 41.5 |

The presence of the unsaturated ketal (I) in the addition products justifies the assumption that the addition of the first molecule of methyl alcohol leads to the formation of a diene ester which is obtained by the addition of the first molecule of alcohol at the triple bond or by addition at the 1,4 position, followed by isomerization into a diene.

The second molecule of methyl alcohol is added to the diene ester, forming the unsaturated ketal (I). The structure of the ketal (I) was proven by its hydrolysis into the unsaturated ketone 2-methyl-1-buten-3-one. The addition of methyl alcohol to the unsaturated ketal (I) may proceed in two directions:



$$(I)\xrightarrow{CH_3OH}\begin{cases}CH_3OCH_2-CH(CH_3)-C(OCH_3)_2-CH_3 & (II)\\ (CH_3)_2C(OCH_3)-C(OCH_3)_2-CH_3 & (IIa)\end{cases}$$

As a result of the hydrolysis of the methoxyketal the ketone $CH_3OCH_2CH(CH_3)-\underset{\underset{O}{\|}}{C}-CH_3$ (III) was obtained and was found to be identical with 1-methoxy-2-methyl-3-butanone, synthesized directly by the addition of methyl alcohol at the double bond of the unsaturated ketone 2-methyl-1-buten-3-one. The isomeric methoxyketone 2-methoxy-2-methyl-3-butanone was described by I. N. Nazarov [1] and its constants are markedly different from the constants of the hydrolysis product of the methoxyketal (II). The addition product of 3 molecules of alcohol and isopropenylacetylene corresponds in structure to the dimethylketal of 1-methoxy-2-methyl-3-butanone (II) and the addition of methyl alcohol to the unsaturated ketal (I), therefore, proceeds in a contrary manner to Markovnikov's rule. The diene ester of 2-methyl-3-methoxy-1,3-butadiene (IV) was obtained by splitting off methyl alcohol from the dimethylketal of 1-methoxy-2-methyl-3-butanone with potassium bisulfate; the structure of this ester was proven by condensing with quinone.

$$\text{(II)} \xrightarrow{CH_3OH} \underset{\text{(IV)}}{CH_2{=}C(CH_3){-}C(OCH_3){=}CH_2}$$

The condensation reaction did not take place at room temperature. We were only able to obtain an addition product when the reagents were heated in a sealed tube for 4 hours at 100°. It is interesting to compare these data with those of L. V. Fedorova [2] for the condensation of cyclic diene esters of $\alpha$-methoxyvinyl-1-cyclohexene and $\alpha$-methoxyvinyl-1-cyclopentene with quinones. These esters have a much greater reactivity in diene synthesis with quinones than the open-chained diene ester (IV) which we obtained.

The condensation of (IV) with sulfur dioxide was of interest to us because of the possibility of the synthesis of a ketosulfone. As a result of a number of experiments we established that the main direction of the reaction is the polymerization of the diene ester (IV) itself. As in the case of the more reactive diene, an attempt to carry out this reaction with $\alpha$-methoxyvinylcyclohexene also lead to the formation of polymerized products of a diene containing only 3 % sulfur.

## EXPERIMENTAL

### Addition of Methyl Alcohol to Isopropenylacetylene

Experiment 1. 1.5 g of red mercuric oxide, 0.5 g of the addition compound of ether and of boron trifluoride, 0.2 g of monochloroacetic acid and 1 ml of methyl alcohol were placed in a 250 ml three-necked flask equipped with a thermometer, stirrer, dropping funnel and reflux condenser which was protected by a calcium chloride tube. The mixture was carefully heated to 50-60° after which 50 ml of methyl alcohol was added to the catalyst; the remainder of the alcohol (20 ml) and 33 g of hydrocarbon were added slowly from the dropping funnel. The reaction temperature was regulated by cooling the flask in a bath of water. After the addition of all the hydrocarbon (1 hour) stirring was continued for a further 8 hours and sodium methylate (0.5 g of sodium in 10 ml of alcohol) was then added to the reaction mixture. The excess alcohol was distilled off and the reaction products were distilled first at atmospheric pressure and then under vacuum.

The following fractions were obtained from the distillation: 1st, 117-120° (760 mm), $n_D^{20}$ 1.4130, 14 g; 2nd, 69° (22 mm), $n_D^{20}$ 1.4170, 20 g.

Investigation of the product with a b.p. of 117-120° (760 mm) — the dimethylketal of 2-methyl-1-buten-3-one (I).

$n_D^{20}$ 1.4130, $d_4^{20}$ 0.8827, $MR_D$ 36.61. $C_7H_{14}O_2$ F Calculated 35.61.

Found %: C 64.40; H 10.52; $OCH_3$ 47.9, 47.7. $C_7H_{14}O_2$. Calculated %: C 64.62; H 10.77; $OCH_3$ 47.7.

Hydrolysis of the product with a b.p. of 117-120° (I). 1 g of the substance (I) was shaken in a test tube with 5 ml of water, acidified with 4 drops of hydrochloric acid. The reaction products were extracted with ether. After the ether had been distilled off 0.7 g of a substance was obtained which gave a semicarbazone with an m.p. of 172-173° (alcohol) [3].

Found %: N 29.75, 29.93. $C_6H_{11}ON_3$. Calculated %: N 29.80.

A mixed melt of the semicarbazone with the semicarbazone of 2-methyl-1-buten-3-one, obtained by the hydration of isopropenylacetylene, showed no depression of the melting point.

### Investigation of the product with a b.p. of 69° (22 mm) — the dimethyl ketal of 1-methoxy-2-methyl-3-butanone (II).

$n_D^{20}$ 1.4175, $d_4^{20}$ 0.9301, $MR_D$ 43.80; calc. 44.07.

Found %: C 59.03, 59.26; H 10.77, 10.21; $OCH_3$ 58.2, 58.0. M 162.9. $C_8H_{18}O_3$. Calculated %: C 59.27; H 11.11; $OCH_3$ 57.41. M 162.

Hydrolysis of the product with a b.p. of 69° (22 mm) (II). 8 g of the product (II) was shaken with 1 ml of distilled water and 2 drops of concentrated hydrochloric acid in a small flask with a ground glass stopper. The ketone was extracted with ether. 3.7 g of a product corresponding to 1-methoxy-2-methyl-3-butanone (III) was obtained.

B. p. 46-47° (18 mm), $n_D^{20}$ 1.4090, $d_4^{20}$ 0.9093, $MR_D$ 31.54; calc. 31.56.

Found %: $OCH_3$ 28.5. 28.6. $C_6H_{12}O_2$. Calculated %: $OCH_3$ 26.72.

The semicarbazone of the methoxyketone was obtained. B. p. 95-96° (petroleum ether).

Found %: N 24.21, 24.50; $OCH_3$ 18.10, 17.78. $C_{17}H_{15}O_2N_3$. Calculated %: N 24.28; $OCH_3$ 17.95.

### Preparation of 1-methoxy-2-methyl-3-butanone [3]

0.6 g of mercuric sulfate, 0.3 ml of concentrated sulfuric acid and 70 ml of anhydrous methyl alcohol were placed in a three-necked reaction flask equipped with two dropping funnels and a reflux condenser. 20 g of isopropenylacetylene and 18 ml of distilled water were then added dropwise simultaneously to the flask. Mercuric sulfate was then added in four lots of 0.6 g each. The temperature of the water bath was maintained at 75-80°. An aqueous solution of alkali and methoxyketone extracted with ether was added to the reaction flask 7 hours after the commencement of the reaction. The b.p. was 144-148° (760 mm), $n_D^{20}$ 1.4110.

Found %: C 62.23, 62.00; H 10.13, 10.10. M 114.5. $C_6H_{12}O_2$. Calculated %: C 62.07; H 10.34. M 116.

The semicarbazone of the methoxyketone was obtained. A mixed melt of a sample of this semicarbazone and the semicarbazone of the hydrolysis product of substance (II) showed no depression of the melting point; product (III) obtained by the hydrolysis of substance (II) was, therefore, really 1-methoxy-1-methyl-3-butanone.

Preparation of 2-methyl-3-methoxy-1,3-butadiene (IV). 0.2 g of potassium bisulfate, previously heated to 202°, was placed in a flask with a fractionating column. The methyl alcohol was split off by distilling the methoxyketal (II) at atmospheric pressure. A 50 % yield of 2-methyl-3-methoxy-1,3-butadiene was obtained.

B. p. 99° (760 mm), $n_D^{20}$ 1.4487, $d_4^{20}$ 0.8457, $MR_D$ 31.06. $C_6H_{10}O_2$ F. Calculated 30.62.

Found %: $OCH_3$ 31.3, 31.6. M 96.9. $C_6H_{10}O$. Calculated %: $OCH_3$ 31.6 M 98.

The addition product with p-benzoquinone was obtained by heating 1.63 g of diene ester with 1 g of quinone and 10 ml of anhydrous benzene in a sealed tube for 4 hours at 100°. The m.p. was 50-52° (petroleum ether).

Found %: C 69.91, 69.97; H 6.82, 6.89; $OCH_3$ 15.5. $C_{12}H_{14}O_3$. Calculated %: C 69.90; H 6.79; $OCH_3$ 15.05.

## SUMMARY

1. Two products — the dimethylketal of 2-methyl-1-buten-3-one and the dimethylketal of 1-methoxy-2-methyl-3-butanone — were obtained in a ratio of 1 : 1 by the action of methyl alcohol on isopropenylacetylene in the presence of $BF_3 \cdot (C_2H_5)_2O$ and HgO at 25°.

2. It was shown that the first two molecules of alcohol are added at the triple bond of the hydrocarbon while the third molecule of alcohol is added at the double bond of the unsaturated ketal, contradictory to Markovnikov's rule.

3. The diene ester 2-methyl-3-methoxy-1,3-butadiene was obtained by splitting off alcohol from the dimethylketal of 1-methoxy-2-methyl-3-butanone.

4. The diene condensation of 2-methyl-3-methoxy-1,3-butadiene with p-benzoquinone was carried out.

## LITERATURE CITED

[1] I. N. Nazarov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 2, 195 (1940).

[2] I. A. Favorskaya and L. V. Fedorova, J. Gen. Chem. 24, 250 (1954).*

[3] I. N. Nazarov and S. A. Vartanyan, J. Gen. Chem. 23, 1986 (1953).*

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* Original Russian pagination. See C.B. Translation.

# SYNTHESIS, CATALYTIC HYDROGENATION AND HYDROGENOLYSIS OF UNSATURATED ETHERS

A. I. Lebedeva and M. M. Monkosha

In previous works it was established by one of the authors together with Almashi [1, 2] that as a result of the catalytic hydrogenation at normal pressure and room temperature of $\gamma,\gamma$-dimethylallyl ethers of dimethylvinylcarbinol (II) and $\gamma,\gamma$-dimethylallyl alcohol (I) in the presence of platinum black the ether bond is ruptured, with the formation of the corresponding amyl alcohols and isopentane. Rupture of the ether bond by catalytically activated hydrogen has hitherto only been noted with benzyl or phenyl ethers [3 - 7].

In the present work it was decided to study the process more accurately and to establish the causes of hydrogenolysis of the ether bond which can usually only be ruptured under fairly drastic conditions.

For this purpose we investigated the process of catalytic hydrogenation of $\gamma,\gamma$-dimethylallyl ethers of $\gamma,\gamma$-dimethylallyl alcohol (I) and dimethylvinylcarbinol (II), isoamyl ethers of $\gamma,\gamma$-dimethylallyl alcohol (III) and dimethylvinylcarbinol (IV). the $\gamma,\gamma$-dimethylallyl ether of tertiary amyl alcohol (V) and the process of hydrogenolysis of the ethers (I), (II) and (V) (see the system of reactions).

We used Pt black, Pd on $CaCO_3$ and Raney Ni as catalysts. It was found that hydrogenolysis of unsaturated ethers on Pt black was only observed in the presence of traces of mineral acids (hydrochloric or hydrobromic). If the hydrogenation process was carried out in a strictly neutral medium no hydrogenolysis took place and the only reaction products were saturated ethers, the diisoamyl (VI) and isoamyl ether of tertiary amyl alcohol (VII). The activating action of acids on the process of catalytic hydrogenation was first noted by Rosenmund, Marcus and Karg [8] who found that the $Ar-CHOH$ group is easily reduced to $Ar-CH_2$ in the presence of $HClO_4$. Other mineral acids act in a similar manner but are less active. Hydrogenation does not take place or does not proceed to completion without the addition of acid. Kinder and Blaas [9] obtained similar results. These authors consider that as a result of the formation of a molecular compound the $C-O-C$ bonds are weakened and the rate and degree of completeness of hydrogenation increased.

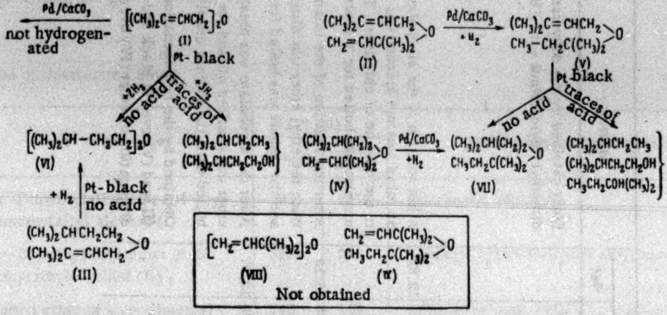
The apparently spontaneous rupture of unsaturated ethers previously noted [1, 2], is evidently explained by the presence of traces of acid in the investigated ether or in the air of the laboratory.

The next series of experiments was carried out with palladium on calcium carbonate. Under these conditions the $\gamma,\gamma$-dimethylallyl ether of dimethylvinylcarbinol (II) added only one molecule of hydrogen with the formation of the $\gamma,\gamma$-dimethylallyl ether of tertiary amyl alcohol (V) which has only one unsaturated bond. The isoamyl ether of dimethylvinylcarbinol (IV) also added one molecule of hydrogen with the formation of the isoamyl ether of tertiary amyl alcohol (VII). The $\gamma,\gamma$-dimethylallyl ether of $\gamma,\gamma$-dimethylallyl alcohol (I) was not hydrogenated in the presence of Pd on $CaCO_3$. As a result of these experiments it was possible to establish the selective relationship of catalytically activated hydrogen in the presence of Pd on $CaCO_3$ toward a different type of double bond of unsaturated ethers. The $>C=CH_2$ bond is quantitatively hydrogenated: under the conditions of the investigation the $(CH_3)_2C=CH$ bond is virtually unaffected.

During hydrogenation with Raney nickel no cessation was observed after the addition of one molecule of hydrogen and the product obtained after the addition of one molecule of hydrogen was clearly nonhomogeneous.

The structure of the initial, intermediate and final products was proven by ozonization, oxidation and hydrogenation to be corresponding ethers and by synthesis. Initially, ethers (I) and (II) were obtained by the dehydrogenation of dimethylvinylcarbinol by an aqueous solution of $KHSO_4$ (10-20 %), the yield being insignificant.

Later, a part of the ethers was obtained by Williamson's reaction [10]. It must be pointed out that in no experiment did we succeed in obtaining the ditertiary α,α-dimethylallyl ether of dimethylvinylcarbinol (VIII). Attempts to obtain this ether by Henry's [11] and Meerwein's method [12] gave negative results.


Pd/CaCO₃
not hydrogenated
[(CH₃)₂C=CHCH₂]₂O
(I)
Pt-black
+2H₂
no acid
traces of acid
+3H₂
[(CH₃)₂CH−CH₂CH₂]₂O
(VI)
(CH₃)₂CHCH₂CH₃
(CH₃)₂CHCH₂CH₂OH
+H₂
Pt-black
no acid
(CH₃)₂CHCH₂CH₂>O
(CH₃)₂C=CHCH₂
(III)
(CH₃)₂C=CHCH₂>O
CH₂=CHC(CH₃)₂
(II)
Pd/CaCO₃
+H₂
(CH₃)₂C=CHCH₂>O
CH₃−CH₂C(CH₃)₂
(V)
Pt black
no acid
traces of acid
(CH₃)₂CH(CH₂)₂>O
CH₂=CHC(CH₃)₂
(IV)
Pd/CaCO₃
+H₂
(CH₃)₂CH(CH₂)₂>O
CH₃CH₂C(CH₃)₂
(VII)
(CH₃)₂CHCH₂CH₃
(CH₃)₂CHCH₂CH₂OH
CH₃CH₂COH(CH₃)₂
[CH₂=CHC(CH₃)₂]₂O
(VIII)
CH₂=CHC(CH₃)₂>O
CH₃CH₂C(CH₃)₂
(IX)
Not obtained

It was not possible to synthesize the α,α-dimethylallyl ether of tertiary amyl alcohol (IX). This failure was not incidental. It is known that systems containing a number of tertiary carbon atoms are not very stable [13]. For example, numerous attempts to synthesize ditertiary butyl ether were not successful before 1941 [14].

## EXPERIMENTAL

Synthesis of unsaturated ethers. 100 g of dimethylvinylcarbinol and 100 ml of 20 % $KHSO_4$ solution were placed in a flask. The temperature of the mixture was raised to 80° with continual stirring whereupon formation of isoprene commenced. Heating was continued for 20 hours after which the upper layer (76 g) was separated, washed with a solution of alkali and dried with calcined potash. A fraction with a b.p. of 30-60° (5 mm) was separated from a mixture boiling within a very wide range (30-105° at 5 mm). The following fractions were obtained from the distillation of 100 g with a fractionating column : 1st, 31.5-33°, 54g; 2nd, 39-40°, 15 g; 3rd, 56-57°, 9 g. From their constants the 1st fraction corresponded to γ,γ-dimethylallyl alcohol, the 2nd to the γ,γ-dimethylallyl ether of dimethylvinylcarbinol (II), the 3rd to the γ,γ-dimethylallyl ether of γ,γ-dimethylallyl alcohol (I).

Synthesis of ethers (II) - (V) by Williamson's method [10]. Equimolecular amounts of metallic sodium, carbinol and the corresponding bromide or chloride were used for each experiment. The metallic sodium was cut into small pieces in toluene and then washed by decantation from ethyl ether. The γ,γ-dimethylallyl bromide was obtained by Mokievsky's method [15]. The mixture of α,α- and γ,γ-dimethylallyl chlorides was obtained by Nazarov's method [16].

The precipitated sodium halide was filtered off and the mixture distilled first from a Favorsky flask and then with a fractionating column. The other conditions of preparation, the constants and the analysis of the ethers obtained are given in Table 1.

Attempts to synthesize the ditertiary ethers (VIII) and (IX). As the result of the action of a mixture of α,α- and γ,γ-dimethylallyl chlorides on the alcoholate of dimethylvinylcarbinol isoprene, ether (II) and the initial compounds were formed. By the action of potash (using Meerwein's method) on a mixture of the chlorides and dimethylvinylcarbinol or a mixture of dimethylvinylcarbinol and tertiary amyl bromide the initial compounds were obtained. By the action of the alcoholate of tertiary amyl alcohol on a mixture of the chlorides and similarly by the action of the alcoholate of dimethylvinylcarbinol on tertiary amyl bromide, only the formation of amylenes was noted. When a mixture of dimethylvinylcarbinol with tertiary amyl iodide and pyridine was heated in sealed tubes pyridine hydrogen iodide and amylene were formed.

Catalytic hydrogenation. Hydrogenation was carried out in an S. V. Lebedev apparatus [17] in a vessel with a capacity of about 250 ml. The amount of solvent (ethyl ether or 96 % alcohol) used was 10 times that of the substance. The weighed samples of the substance varied from 1-10 g.

TABLE 1

Methods of Preparation, Constants and Analyses of Unsaturated Ethers

| Name of ether | Initial reagents | Boiling point | Yield (in %) | $n_D^{20}$ | $d_4^{20}$ | Found * |  |  | Remarks |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | $MR_D$ | %C | %H |  |
| γ,γ-Dimethylallyl ether of γ,γ-dimethylallyl alcohol (I) | Dimethylvinylcarbinol | 74°(8 mm) | – | 1.4517 | 0.8412 | 49.43 | – | – | Ether obtained by the dehydration of dimethylvinylcarbinol with $KHSO_4$. |
| γ,γ-Dimethylallyl ether of dimethylvinylcarbinol (II) | Dimethylvinylcarbinol<br>γ,γ-dimethylallyl bromide | 43 (4 mm) | 65 | 1.4401 | 0.8246 | 49.30 | – | – | – |
| Isoamyl ether of γ,γ-dimethylallyl alcohol (III) | Isoamyl alcohol.<br>Mixture of chlorides obtained by Nazarov's method | 60 (7 mm) | 52 | 1.4283 | 0.8046 | 49.33 | 76.60 | 12.82 | A hot solution of the alcoholate in 50 ml of isoamyl alcohol was added to the mixture of chlorides. The mixture was boiled for 3 hours |
| Isoamyl ether of dimethylvinylcarbinol (IV) | Dimethylvinylcarbinol.<br>Isoamyl bromide | 48 (12 mm) | 9 | 1.4142 | 0.7876 | 49.39 | 76.88 | 13.13 | After the addition of the isoamyl bromide the ethyl ether was distilled off and the residue was boiled for 5 hours |
| γ,γ-Dimethylallyl ether of tertiary allyl alcohol (V) | Tertiary amyl alcohol.<br>γ,γ-Dimethylallyl bromide | 48-50 (5 mm) | 70 | 1.4318 | 0.8140 | 49.12 | 76.99 | 12.97 | After the alcoholate was obtained the ether was distilled off and the mixture boiled until the sodium dissolved. |
| Isoamyl ether of tertiary amyl alcohol (VII) | – | 160 | – | 1.4085 | 0.7824 | – | – | – | Obtained by the hydrogenation of ethers (II) and (V) over Pt black and by the hydrogenation of ether (IV) over Pd on $CaCO_3$ |

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* $C_{10}H_{18}O$. Calculated: $MR_D$ 49.09.

$C_{10}H_{20}O$. Calculated: $MR_D$ 49.56; %: C 76.84; % H 12.09.

The amount of catalyst used was generally 10 % by weight of the substance. After hydrogenation the catalyst was filtered off, the solvent was evaporated and the substance was distilled and analyzed. The Pt black was prepared by the Fokine-Willstatter method [18]. The Pd on $CaCO_3$ was prepared by the Busch-Steve method [19] and the skeletal nickel catalyst by the Covert and Adkins method [20]. The data of the experiments on hydrogenation without rupture are given in Table 2.

TABLE 2

Hydrogenation of Unsaturated Ethers

| Expt. No. | Name of the ether | H (in ml) Found | H (in ml) Calculated | Final product of hydrogenation |
|---|---|---|---|---|
| 1 | γ,γ-Dimethylallyl ether of γ,γ-dimethylallyl alcohol (I) | 297 | 291 | Diisoamyl ether (VI) |
| 2 | γ,γ-Dimethylallyl ether of dimethylvinylcarbinol (II) | 305 | 291 | Isoamyl ether of tertiary amyl alcohol (VII) |
| 3 | Isoamyl ether of γ,γ-dimethylallyl alcohol (III) | 142 | 143 | Diisoamyl ether (VI) |
| 4 | γ,γ-Dimethylallyl ether of tertiary amyl alcohol (V) | 154 | 143 | Isoamyl ether of tertiary amyl alcohol (VII) |
| 5 | γ,γ-Dimethylallyl ether of dimethylvinylcarbinol (II) | 158 | 145 | γ,γ-Dimethylallyl ether of tertiary amyl alcohol (V) |
| 6 | Isoamyl ether of dimethylvinylcarbinol (IV) | 141 | 143 | Isoamyl ether of tertiary amyl alcohol (VII) |
| 7 | γ,γ-Dimethylallyl ether of γ,γ-dimethylvinylcarbinol (I) | 230 | 143 | Not analyzed |
| 8 | γ,γ-Dimethylallyl ether of dimethylvinylcarbinol (II) | 875 | 861 | Mixture of ethers in which ~ 20% of the initial ether remained. |

Note: Catalyst: Pt black for experiments 1-4, Pd on $CaCO_3$ for experiments 5-6 and Raney nickel for experiments 7-8.

TABLE 3

Hydrolytic Rupture of Unsaturated Ethers

| Expt. No. | Name of the ether. | Weighed sample (in g) | H (in ml) Found | H (in ml) Calculated | Final product of hydrogenolysis |
|---|---|---|---|---|---|
| 1 | γ,γ-Dimethylallyl ether of dimethylallyl alcohol (I) | 2.0 | 870 | 872 | Isopentane, isoamyl alcohol |
| 2 | γ,γ-Dimethylallyl ether of dimethylvinylcarbinol (II) | 11.6 | 5245 | 5055 | Isopentane, isoamyl alcohol, tertiary amyl alcohol |
| 3 | γ,γ-Dimethylallyl ether of tertiary amyl alcohol (V) | 4.0 | 1030 | 1148 | Isopentane, tertiary amyl alcohol |

1 g of the substance was used in the first seven experiments and 6 g in experiment 8. In the latter experiment hydrogenation was stopped after the addition of one molecule of hydrogen, the solution was filtered and the filtrate divided into two equal parts. One half was hydrogenated over Pt black (470 ml of hydrogen was absorbed), the other half was hydrogenated over Pd/$CaCO_3$, 89 ml of hydrogen being absorbed (20 % of the theoretical, on the basis of 1 mole of hydrogen).

Ozonization and oxidation of the γ,γ-dimethylallyl ether of tertiary amyl alcohol (V). 1.9 g of the ether (V) and 20 g of chloroform were used. 0.690 g of ozone was absorbed. Acetone in the form of its 2,4-dinitrophenylhydrazone was found in the products of ozonolysis. Formaldehyde and formic acid were absent.

Acetone 2,4-dinitrophenylhydrazone was obtained from the neutral distillate when 1.9 g of the ether (V) was oxidized with 4.5 g of $KMnO_4$.

The hydrolytic rupture of the ethers was carried out by hydrogenation over Pt black in the presence of one or two drops of dilute (1 : 100) HCl or HBr. All the other experimental conditions were unchanged. The results of hydrogenation are given in Table 3. The amount of hydrogen absorbed was calculated on the basis of 3 moles of hydrogen in experiments 1 and 2 and 2 moles in experiment 3. It was not possible to detect isoamyl alcohol in the hydrogenolysis products of the γ,γ-dimethylallyl ether of tertiary amyl alcohol (experiment 3).

## SUMMARY

1. The reaction of the catalytic hydrogenation and hydrogenolysis of unsaturated ethers with the general formulas $C_{10}H_{18}O$ and $C_{10}H_{20}O$ was investigated.

It was found that in an absolutely neutral medium over Pt black only hydrogenation of unsaturated ethers, with formation of the corresponding saturated ethers, takes place.

2. It was established that in the presence of traces of acid, diolefin ethers containing double bonds in the β-position to the ether bond undergo rupture of the ether bond, together with hydrogenation, with formation of the corresponding hydrocarbons and alcohols. In the case of unsaturated ethers with only one double bond hydrogenolysis does not proceed to completion.

3. A selective relationship of catalytically activated hydrogen in the presence of Pd on $CaCO_3$ toward a different type of bond in the investigated ethers was noted. The $(CH_3)_2C{=}CH$ bond is virtually unaffected, the $CH_2{=}CH$ bond is completely hydrogenated.

4. 4 new ethers were obtained during the investigation: the isoamyl ether of γ,γ-dimethylallyl alcohol, the isoamyl ether of dimethylvinylcarbinol, the γ,γ-dimethylallyl ether of tertiary amyl alcohol and the isoamyl ether of tertiary amyl alcohol.

## LITERATURE CITED

[1] A. I. Lebedeva and L. F. Almashi, Proc. Acad. Sci. USSR 86, 75 (1952).

[2] A. I. Lebedeva and L. F. Almashi, J. Gen. Chem. 23, 994 (1953).[*]

[3] V. N. Ipatyev and Lugovoi, J. Phys. Chem. Soc. 46, 470 (1914).

[4] E. M. Van Duzee and H. Adkins, J. Am. Chem. Soc. 57, 147 (1935).

[5] M. Tomita and S. Uyeo, J. Chem. Soc. Japan, 63, 1189 (1942); Ch. A. 41, 4121 (1947).

[6] C. J. Cavalito and J. S. Buck, J. Am. Chem. Soc. 65, 2140 (1943).

[7] R. H. Baker, K. H. Cornell and M. J. Cron, J. Am. Chem. Soc. 70, 1490 (1948).

[8] K. W. Rosenmund, E. Karg and F. K. Marcus, Ber. 75, 1850 (1942); Ch. A. 38, 1219 (1944).

[9] K. Kindler and L. Blaas, Ber. 76, 1211 (1943); Ch. A. 39, 288 (1945).

[10] A Williamson, Lieb. Ann. 77, 37 (1851); 81, 73 (1852).

[11] L. Henry, Bull. Acad. roy. Belg. 1904, 42.

[12] H. Meerwein and L. Gerard, Lieb. Ann. 435, 174 (1923).

[13] H. C. Brown and co-workers J. Am. Chem. Soc. 75, 1 (1953).

[14] J. L. Erickson and W. H. Ashton, J. Am. Chem. Soc. 63, 1769 (1941).

[15] V. A. Mokievsky, J. Phys. Chem. Soc. 32, 212 (1900).

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[*] Original Russian pagination. See C.B. Translation.

[16] I. N. Nazarov and I. N. Azerbaev, J. Gen. Chem. 18, 414 (1948).

[17] S. V. Lebedev, Life and Works. Leningrad [In Russian] (1938), 381.

[18] V. Hickinbottom, Reactions of Organic Compounds, [Russian Translation], GONTI, 24 (1939).

[19] I. Houben, Methods of Organic Chemistry, [Russian Translation], II, Book 1, 497 (1941).

[20] L. W. Covert and H. Adkins, J. Am. Chem. Soc. 54, 4116 (1932).

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# INVESTIGATIONS IN THE FIELD OF POLYMETHYLENE RING SYSTEMS

## XXIX. THE REACTIONS AND REACTION PRODUCTS OF CYCLIC, ALIPHATIC AND ALIPHATIC-AROMATIC 1,3-DIKETONES WITH HYDRAZINE AND SUBSTITUTED HYDRAZINES

N. A. Domnin, Van Syui-Kun and V. A. Cherkasova

We showed [1] that cyclohexane-1,3-dione and 5,5-dimethylcyclohexane-1,3-dione (dimedone) give only products of uncertain structure instead of the expected mono- and dihydrazones when reacted with hydrazine hydrate.

When reacted with dimethylhydrazine both these ketones give only monodimethylhydrazones but not bis-dimethylhydrazones. Under these conditions the aliphatic 1,3-diketone, acetylacetone, which has a similar structure, gives a monohydrazone and 3,5-dimethylpyrazole with hydrazine but with dimethylhydrazine readily gives both a monomethylhydrazone and a bis-dimethylhydrazone. We explained this difference in the behavior of cyclic and aliphatic 1,3-diketones when reacted with hydrazine and dimethylhydrazine on the basis of the different structure of the initial diketones and the steric hindrances arising in the case of the formation of cyclic hydrazones.

In order to extend the above-mentioned considerations it was of interest to compare the behavior of aliphatic and aliphatic-aromatic 1,3-diketones in reactions with hydrazine and substituted hydrazines. For this comparative investigation we used acetylacetone and dibenzoylmethane, as being the simplest representatives of aliphatic and aliphatic-aromatic 1,3-diketones. As a rough qualitative hypothesis we assumed that in dibenzoylmethane monodimethylhydrazone the two phenyl groups and the radical of the molecule of substituted hydrazine which has reacted with the first carbonyl group would hinder the approach of the second molecule of substituted hydrazine to the second carbonyl group of dibenzoylmethane. In accordance with these considerations it would be expected that with substituted hydrazines acetylacetone would give both mono- and dihydrazones while dibenzoylmethane would only give monohydrazones. The possibility of closure of the pryrazole ring is eliminated in this instance because of the absence in substituted hydrazine molecules of active hydrogen atoms which could be liberated in the form of water with the oxygen of the carbonyl group of dibenzoylmethane.

| Reagent used | Reaction Products* | |
|---|---|---|
| | With acetylacetone | With dibenzoylmethane |
| Hydrazine hydrate | 3,5-Dimethylpyrazole [2], monohydrazone hydrate | 3,5-Diphenylpyrazole [3] |
| Dimethylhydrazine | Monodimethylhydrazone, bis-dimethylhydrazone | Monodimethylhydrazone |
| Acethydrazide | Diacethydrazone | Monoacethydrazone |
| Semicarbazide | Carboamidopyrazole [4], disemicarbazone | Carboamidopyrazole [4], monosemicarbazone [5] |
| 4-Nitrophenylhydrazine | 1,3,5-Substituted pyrazole [6] | Unknown |
| 2,4-Dinitrophenylhydrazine | Mono- and bis-2,4-dinitrophenylhydrazone [7] | Mono-2,4-dinitrophenylhydrazone |

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* Substances without literature references were obtained by us for the first time.

The data we obtained and those of other investigators are given in Table 1. All these data are in agreement with our considerations mentioned above.

As may be seen from the data in Table 1, acetylacetone with dimethylhydrazine, acethydrazide, semicarbazide and 2,4-dinitrophenylhydrazine gives both mono- and dihydrazones while dibenzoylmethane gives only monohydrazones. Of the mono- and dihydrazones given in Table 1, 8 were obtained by us for the first time.

## EXPERIMENTAL

Diacethydrazone of acetylacetone. 3 g of acetylacetone in 15 ml of anhydrous alcohol was added to a solution of 4.5 g of acethydrazide in 45 ml of anhydrous alcohol, the mixture being stirred and cooled with ice water. When the solvent had been removed the thick oil remaining crystallized out after a period of 3 weeks. After recrystallizing from benzene 2 g of the pure substance was obtained in the form of plates. The yield was 31%. The m.p. was 124-126°.

Found %: N 26.41, 26.19. M 208.8, 214 (according to Rast). $C_9H_{16}O_2N_4$. Calculated %: N 26.41. M 212.

Disemicarbazone of acetylacetone. An aqueous-alcoholic solution of semicarbazide was obtained from 0.5 g of semicarbazide hydrochloride, 0.5 g of potassium acetate, 5 ml of water and 5 ml of alcohol. 0.2 g of acetylacetone in 2 ml of alcohol was mixed with this solution. The disemicarbazone precipitated out over a period of two days. It was recrystallized from aqueous alcohol. The m.p. was 234°.

Found %: N 38.94, 39.00. M 208, 210 (according to Rast). $C_7H_{14}O_2N_6$. Calculated %: N 39.25. M 214.

Monomethylhydrazone of dibenzoylmethane. Dibenzoylmethane was obtained from ethyl benzoate and acetophenone with metallic sodium by the Claisen method [8]. The reaction mixture was treated according to the method described in literature [9].

Dibenzoyl methane reacts with dimethylhydrazine in the cold when left for 6-7 days or when heated for 1.5-2 hours at about 150°. Only a monodimethylhydrazone was formed as a result of this reaction. The product was recrystallized twice from ethyl alcohol and dried in a vacuum desiccator. The m.p. was 112-113°.

Found %: N 10.73, 10.62. $C_{17}H_{18}ON_2$. Calculated %: N 10.77.

Dibenzoylmethane was heated for several hours at 200° with a large excess of dimethylhydrazine. After extraction and purification the product was found to be a monodimethylhydrazone. The m.p. was 112-113°.

Found %: N 11.05, 10.70. $C_{17}H_{18}ON_2$. Calculated %: N 10.77.

Dibenzoylmethane, therefore, reacts with only one molecule of dimethylhydrazine and does not react at all with a second molecule.

Monoacethydrazone of dibenzoylmethane. A solution of 2 g of dibenzoylmethane in 10 ml of chloroform was mixed with a solution of 2 g of acethydrazine in 10 ml of chloroform and heated at 100° for 1 hour. The precipitated crystals were recrystallized from ethyl alcohol. The m.p. was 125-126°.

Found %: N 9.79, 9.84. $C_{17}H_{16}O_2N_2$. Calculated %: N 10.00.

Mono-2,4-dinitrophenylhydrazone of dibenzoylmethane. A solution of 0.4 g of dibenzoylmethane in 10 ml of alcohol was mixed with a prepared solution of 0.8 g of 2,4-dinitrophenylhydrazine. The precipitated crystals were recrystallized from a mixture of ethyl acetate and ethyl alcohol. The m.p. was 149-150°.

Found %: N 14.25, 13.88. $C_{21}H_{16}O_5N_4$. Calculated %: N 13.86.

The action of hydrazine hydrate on the monodimethylhydrazone of dibenzoylmethane. 2 g of the monodimethylhydrazone of dibenzoylmethane was heated with 2 g of hydrazine hydrate at 150° for 2.5 hours. When heated the hydrazone formed first dissolved in the hydrazine hydrate, then white crystals were precipitated; these were recrystallized from ethyl alcohol. The crystals obtained were in the form of plates. The m.p. was 199-200°. A mixed melt of a sample of the crystals with 2,5-dimethylpyrazole showed no depression of the melting point.

Found %: N 13.00, 12.93. $C_{15}H_{12}N_2$. Calculated %: N 12.73.

## SUMMARY

1. The diacethydrazone and disemicarbazone of acetylacetone, the monodimethylhydrazone, monoacethydrazone and mono-2,4-dinitrophenylhydrazone of dibenzoylmethane were synthesized and characterized for the first time.

2. It was found that dibenzoylmethane gives only monhydrazones with the substituted hydrazines listed above and does not give dihydrazones.

3. It was shown that when heated with hydrazine hydrate the monodimethylhydrazone of dibenzoylmethane gives 3,5-dimethylpyrazole.

4. An attempt was made to explain the facts obtained in accordance with theories of steric hindrance.

## LITERATURE CITED

[1] N. A. Domnin and N. S. Glebovskaya, J. Gen. Chem. 27, 656 (1957).*

[2] Knorr, Lieb. Ann. 279, 189, 237 (1894).

[3] Knorr, Duaen, Ber. 26, 116 (1893).

[4] Posner, Ber. 34, 3973 (1901).

[5] Wislicenus, Lieb. Ann. 308, 248 (1899).

[6] Auwers, Ber. 58, 1881 (1925).

[7] Schreiner and Fuson, Systematic Qualitative Analysis of Organic Compounds [Russian Translation] Moscow, p. 259 (1950).

[8] Claisen, Lieb. Ann. 291, 52 (1896).

[9] Synthesis of Organic Compounds, Vol. III, p. 167 (1952).**

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* Original Russian pagination. See C.B. Translation

** In Russian.

# SYNTHESIS OF ω-AMINOCARBOXYLIC ACIDS FROM α,α,α,ω-TETRACHLOROALKANES

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ω-Aminocarboxylic acids are of great interest for the preparation of polyamide fiber. Only the lactam of ω-aminocaproic acid and ω-aminoundecanoic acid have, however, found practical application. Until recently other amino acids of this type, containing more than 6 carbon atoms in the molecule, were found to be difficult to obtain. The present article describes methods of synthesizing a number of ω-aminocarboxylic acids from easily-obtainable tetrachloroalkanes, with the structure $CCl_3(CH_2CH_2)_nCl$, which may be obtained by polymerization of ethylene and carbon tetrachloride.

ω-Aminocarboxylic acids with an odd number of carbon atoms in the molecule may be obtained from tetrachloroalkanes in two stages according to systems 1 or 2.

$$1)\quad Cl(CH_2CH_2)_nCCl_3 \longrightarrow Cl(CH_2CH_2)_nCO_2H \longrightarrow NH_2(CH_2CH_2)_nCO_2H$$

$$2)\quad Cl(CH_2CH_2)_nCCl_3 \longrightarrow NH_2(CH_2CH_2)_nCCl_3 \longrightarrow NH_2(CH_2CH_2)_nCO_2H$$

The study of these reactions showed that the first method has advantages over the second. The disadvantages of the second method include the instability of α,α,α-trichloro-ω-aminoalkanes which become tarry when kept for a short time and, in addition, the necessity of carrying out ammonolysis in the medium of an organic solvent. High yields of amino acids with 7, 9 and 11 carbon atoms were obtained by method 1.

The lower tetrachloroalkanes with 3 to 11 carbon atoms are hydrolyzed by concentrated sulfuric acid when heated, giving a good yield of the corresponding ω-chlorocarboxylic acids [1 - 3]. To hydrolyze higher compounds having this structure considerably more rigid conditions are required, as a result of which secondary processes take place and the yield of the acids falls [3]. To hydrolyze the trichloromethyl group in this instance the best results are obtained by heating with nitric acid (d 1.51-1.52) at 50-60° [4].

Hydrolysis with perchloric acid [5] can be of value for preparing acids containing an aromatic ring because when concentrated sulfuric or fuming nitric acid is used the reaction is frequently complicated by sulfonation or nitration of the ring.

The ammonolysis of ω-haloidcarboxylic acids is generally carried out by infusing with ammonia for a period of several days. For example, according to a patent [6] the ammonolysis of 9-haloidnonanoic acid is carried out by the action of 25 % ammonia at 0-25° for 6-20 days. We found that the higher ω-chlorocarboxylic acids react very rapidly with aqueous 25% ammonia when heated to 100°. The only by-products formed during the ammonolysis of ω-chlorocarboxylic acids are iminodicarboxylic acids $HN[(CH_2)_nCOOH]_2$. The addition of ammonium salts $[NH_4Cl, NH_4NO_3, (NH_4)_2CO_3, NH_4HCO_3]$ to the reaction mixture leads to an increase in the yield of ω-aminocarboxylic acids. An increase in the relative amount of 25 % ammonia also leads to a reduction in the iminodicarboxylic acid content in the reaction product; with a 60-fold excess of ammonia the amount of imino acid formed is very slight.

The isolation [7] of the amino acids from the ammonium chloride was carried out by means of the Soviet-made SBS [8], SDV [8] and KU-2 ion-exchange resins.

New polyamide fibers, called "Enant" and "Pelargon" [9, 10], were obtained from ω-aminoenanthic and ω-aminopelargonic acids, synthesized by this method.

Only a low yield of δ-aminovalerianic acid is obtained by the ammonolysis of δ-chlorovalerianic acid. When heated to 230-250° chlorovalerianic acid and liquid ammonia give α-piperidone [11]. α-Piperidone is also obtained by heating ethyl δ-chlorovalerianate with an alcoholic solution of ammonia at 120-140°.

The synthesis of ω-aminocarboxylic acids with an even number of carbon atoms in the molecule may be carried out according to system 3:

$$3)\quad Cl(CH_2CH_2)_nCCl_3 \longrightarrow CN(CH_2CH_2)_nCCl_3 \longrightarrow NH_2CH_2(CH_2CH_2)_nCCl_3 \longrightarrow NH_2CH_2(CH_2CH_2)_nCO_2H$$

This method presents definite difficulties during the reduction stage of the cyanotrichloroalkanes since the $CCl_3$ group is also partially involved in the reaction.

8-Aminooctanoic and 10-aminodecanoic acid were obtained according to system 4.

$$4)\quad Cl(CH_2CH_2)_nCH_2CH{=}CCl_2 \longrightarrow CN(CH_2CH_2)_nCH_2CH{=}CCl_2 \longrightarrow NH_2CH_2(CH_2CH_2)_nCH_2CH{=}CCl_2 \longrightarrow NH_2(CH_2CH_2)_{n+1}CH_2CO_2H$$

Trichloroalkenes were obtained by catalytic dehydrochlorination in the presence of ferric chloride [12]. In the example of 1,1,1,9-tetrachlorononane we found that dehydrochlorination of the higher tetrachloroalkanes in the presence of antimony pentachloride gives the best yields.* The introduction of a nitro group was carried out in a medium of methyl cellosolve. The cyanodichloroalkenes were reduced by the action of equimolecular amounts of lithium aluminum hydride. The aminodichloroalkenes were hydrolyzed by heating with concentrated sulfuric acid. All these processes give a high yield of the products.

As was shown earlier [3], 8-aminooctanoic acid can also be obtained from 7-chloroheptanoic acid according to system 5:

$$5)\quad Cl(CH_2CH_2)_3CCl_3 \longrightarrow Cl(CH_2CH_2)_3CO_2H \longrightarrow CN(CH_2CH_2)_3CO_2H \longrightarrow NH_2(CH_2)_7CO_2H$$

## EXPERIMENTAL

α-Piperidone. a) From δ-chlorovalerianic acid. 50 g of δ-chlorovalerianic acid and 40 ml of liquid ammonia were heated in a rotary autoclave for 10 hours at 230-250°. After removal of the excess ammonia the residue was treated with dichloroethane to dissolve the α-piperidone. The ammonium chloride was filtered off from the solution and after distillation of the solvent the residue was distilled under vacuum. 34.5 g (93 %) of α-piperidone was obtained; the b.p. was 128-130° at 10 mm, the m.p. was 39-40°. Data in literature give the m.p. as 39-40°.

b) From ethyl δ-chlorovalerianate. A solution of 45 g of ethyl δ-chlorovalerianate and 13 g of ammonia in 90 ml of ethyl alcohol was heated in an autoclave for 3 hours at 120-140°. The product was isolated as described above. 32.2 g (86 %) of α-piperidone was obtained.

ω-Aminoenanthic acid. a) 50 g of chloroenanthic acid in 500 ml of 25 % ammonia water containing 114 g of ammonia (22 moles per mole of chloro acid) was placed in a 600 ml stainless steel autoclave. The autoclave was heated for 2 hours at 100°. After evaporation of the ammonia the solution passed through a column containing a cation exchange resin. The resin was washed out from the chloride ion water and the amino acid was eluted with a 5 % solution of ammonia. The resin was regenerated with a 6 % hydrochloric acid solution. The eluate was evaporated to dryness. 40 g of dry residue was obtained, treated with 40 ml of cold water and then filtered from the undissolved iminoenanthic acid (4.3 g, 10 %). After the filtrate had been decolorized by boiling with activated carbon it was evaporated and the aminoenanthic acid was crystallized from aqueous alcohol. The yield of ω-aminoenanthic acid with an m.p. of 190-191° was 31.8 g (72 %). A further 1.4 g of amino acid was obtained from the mother liquor.

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* The dehydrochlorination of the lower tetrachloroalkanes by means of $SbCl_5$ was developed by N. A. Semenov.

b) Under similar conditions 12.9 g of dry residue was obtained from 15 g of chloro acid and 450 ml of 25% ammonia solution (62 moles per mole of chloro acid). After treatment as described in the previous experiment 11.3 g (86 %) of ω-aminoenanthic acid with an m.p. of 190-191° and 6 % of crude iminodienanthic acid were obtained.

c) 25 g of chloroenanthic acid, 250 ml of 25 % ammonia solution (22 moles per mole of chloro acid) and 58 g of ammonium carbonate (4 moles per mole of chloro acid) heated at 55-60° for 4 hours gave 20.6 g of dry residue from which 17.6 g (80 %) of aminoenanthic acid with an m.p. of 188-189° and 5 % of iminodienanthic acid were isolated. A further 1.1 g of aminoenanthic acid with an m.p. of 175-180° was obtained from the mother liquor.

After repeated recystallization from aqueous alcohol the ω-aminoenanthic acid melted at 194-195°. Data in literature [14] give the m.p. as 195°.

Found %: N 9.82, 9.90. $C_7H_{15}O_2N$. Calculated %: N 9.65.

ω-Aminoenanthic acid is a white crystalline substance readily soluble in water and insoluble in alcohol, acetone and other usual organic solvents. The primary amino group in the acid was determined by Van-Sleyk's method; for this purpose only a slightly longer period of reaction with nitric acid (5-6 minutes) than that used for determining the amino group in α-amino acids is necessary. The amino group was determined qualitatively by reacting with ninhydrin under usual conditions. The chlorohydrate of ω-aminoenanthic acid melted at 99-100° (from a mixture of alcohol and ether). Data in literature [15] give the m.p. as 97-99°.

**ω-Aminopelargonic acid.** 14.8 g (82.5 %) of 9-aminononanoic acid with an m.p. of 185-186° and 1.5 g (8.5 %) of iminodipelargonic acid were obtained from 20 g of 9-chlorononanoic acid and 500 ml of 25 % aqueous ammonia (60 moles per mole of chloro acid) by heating for 1 hour at 100° with subsequent treatment of the reaction mixture as described in the case of aminoenanthic acid. After the amino acid had been recrystallized once from water it melted at 189-190°. ω-Aminopelargonic acid is a white crystalline substance soluble in hot water but insoluble in the usual organic solvents. The methods for the quantitative and qualitative determination of the amino group mentioned for ω-aminoenanthic acid are also applicable for ω-aminopelargonic acid.

Found %: N 7.91, 7.86 (by Van-Sleyk's method). $C_9H_{19}O_2N$. Calculated %: N 8.09.

**11-Aminoundecanoic acid.** The ammonolysis of 11-chloroundecanoic acid was carried out in glass ampoules. A solution of 14 g of 11-chloroundecanoic acid in a 40-fold excess of 40 % aqueous ammonia was left in a sealed ampoule for 48 hours at room temperature. The precipitated aminoundecanoic acid was filtered, washed with water to remove ammonium chloride and recrystallized. The amino acid melted at 185-186°. Data in literature [14] give the m.p. as 186-187°.

**1,1-Dichloro-6-amino-1-hexene.** A solution of 32.8 g (0.2 mole) of 1,1-dichloro-5-cyano-1-pentene in 2 200 ml of absolute ether was added dropwise to 210 ml of a 1-molar solution of lithium aluminum hydride in ether. The reaction mixture was stirred for a further 1 hour at room temperature and then carefully decomposed with water. After 200 ml of 6 N sulfuric acid had been added (to dissolve the aluminum hydroxide) the reaction mixture separated into three layers. Both the lower layers were treated with alkali until they gave a strongly alkaline reaction. The precipitated amine was extracted with ether and dried over potash. After evaporation of the solvent and distillation under vacuum 30.6 g (91 %) of 1,1-dichloro-6-amino-1-hexene was obtained:

b.p. 81-82° at 6 mm, $n_D^{20}$ 1.4868, $d_4^{20}$ 1.1336. Data in literature [16]: b.p. 83-84° at 6 mm, $n_D^{20}$ 1.4865, $d_4^{20}$ 1.1331.

The N-phthalyl derivative had an m.p. of 57-58° (from alcohol).

Found %: C 56.44, 56.26; H 4.45, 4.43; Cl 23.40, 23.38. $C_{14}H_{13}O_2NCl_2$. Calculated %: C 56.39; H 4.49; Cl 23.70.

**1,1-Dichloro-8-amino-1-octene.** The experiment was carried out in a similar manner to the previous experiment. 17.8 g (91 %) of 1,1-dichloro-8-amino-1-octene was obtained from 19.2 g (0.1 mole) of 1,1-dichloro-7-cyano-1-heptene in 100 ml of absolute ether and 105 ml of a 1-molar solution of lithium aluminum hydride in ether:

b.p. 72° at 1.5 mm, $n_D^{20}$ 1.4840, $d_4^{20}$ 1.0765, MR 52.12; Calc. 51.84

Found %: C 48.79, 48.94; H 7.80, 7.72; N 7.23, 7.15. $C_8H_{15}NCl_2$. Calculated %: C 48.98; H 7.71; N 7.14.

The N-phthalyl derivative had an m.p. of 51-52° (from alcohol).

Found %: C 58.63. 58.60; H 5.32, 5.27. $C_{16}H_{17}O_2NCl_2$. Calculated %: C 58.89; H 5.25.

8-Aminooctanoic acid. 35 g of 1,1-dichloro-8-amino-1-octene was added with stirring to 200 g of sulfuric acid (d 1.82). Hydrolysis commenced immediately and proceeded with evolution of heat. To complete the reaction the solution was heated for 30 minutes at 60-65°. The reaction mixture was poured on to ice and part of the sulfuric acid was precipitated with barium oxide (31 g of barium oxide was added). The precipitate was filtered and washed with water until no qualitative reaction with ninhydrin was obtained. The filtrate was neutralized with 25 % ammonia. The isolation of the amino acid was carried out by means of a KU-2 cation exchange resin, as described above. The yield of 8-aminooctanoic acid was 24.5 g (86 %), the m.p. was 190°. After it had been recrystallized from water the m.p. was 192-192.5°. Data in literature [3] give the m.p. of 8-aminooctanoic acid as 187-188°.

Found %: C 60.57, 60.41; H 10.58, 10.91. $C_8H_{17}O_2N$. Calculated %: C 60.36; H 10.76.

1,1,9-Trichloro-1-nonene. 20 ml of antimony pentachloride was added in stages to 320 g of 1,1,1,9-tetrachlorononane with stirring at a temperature of 80°. To complete the reaction the temperature was raised to 100°. The reaction mixture was dissolved in chloroform and washed free from antimony salts with hydrochloric acid and water. The chloroform solution was dried over $CaCl_2$ and the chloroform was evaporated off. After distillation under vacuum 230 g (82 %) of 1,1,9-trichloro-1-nonene was obtained:

b.p. 92° at 1.5 mm, $n_D^{20}$ 1.4836, $d_4^{20}$ 1.1338. Data in literature [12]: b.p. 91-92° at 1.5 mm, $n_D^{20}$ 1.4834; $d_4^{20}$ 1.1342.

1,1-Dichloro-9-cyano-1-nonene. 65 g of trichlorononene, a solution of 20.5 g of sodium cyanide in 50 ml of water and 200 ml of methyl cellosolve were heated with stirring for 12 hours at 120°. The methyl cellosolve was then distilled off and water added to the residue to dissolve the salts. The oil which was precipitated was extracted with chloroform. The chloroform solution was washed twice with water and dried over calcium chloride. After distillation under vacuum 51 g (90 %) of dichlorocyanononene was obtained:

b.p. 122-123° at 2 mm, $n_D^{20}$ 1.4777, $d_4^{20}$ 1.0864, MR 57.33; Calc. 57.46.

Found %: C 54.43, 54.27; H 6.82, 6.80. $C_{10}H_{15}NCl_2$. Calculated %: C 54.54; H 6.87.

1,1-Dichloro-10-amino-1-decene. The experiment was carried out in the same way as that for the preparation of 1,1-dichloro-8-amino-1-octene. 19.3 g (87 %) of 1,1-dichloro-10-amino-1-decene was obtained after appropriate treatment and distillation under vacuum from 22 g (0.1 mole) of 1,1-dichloro-9-cyanononene and 105 ml of a 1-molar solution of lithium aluminum hydride in ether:

b.p. 97-98° at 1.5 mm, $n_D^{20}$ 1.4820; $d_4^{20}$ 1.0425, MR 61.30; Calc. 61.08.

Found %: C 53.45, 53.54; H 8.56, 8.66; Cl 31.29, 31.35. $C_{10}H_{19}NCl_2$. Calculated %: C 53.57; H 8.54; Cl 31.63.

10-Aminodecanoic acid. A solution of 34 g of 1,1-dichloro-10-amino-1-decene in 200 g of sulfuric acid (d 1.82) was heated with stirring for 45 minutes. The isolation of the acid was carried out in the same way as that described for 8-aminooctanoic acid. 23 g (84 %) of aminodecanoic acid with an m.p. of 188° was obtained. After it had been recrystallized from water the m.p. was 189.5-190°. Data in literature [17] give the m.p. as 187-188°.

Found %: C 64.06, 64.10; H 11.24, 11.25. $C_{10}H_{21}O_2N$. Calculated %: C 64.15; H 11.30.

## LITERATURE CITED

[1] H. Prins, J. pr. Ch. 89, 414 (1914).

[2] R. M. Joyce, W. E. Hanford and J. Harmon, J. Am. Chem. Soc. 70, 2529 (1948); Amer. Pat. 2440800; Ch. A. 42, 6373 (1948); Brit. Pat. 581899; Ch. A. 41, 3477 (1947); Amer. Pat. 2398430; Ch. A. 40, 3768 (1946).

[3] A. N. Nesmeyanov, L. I. Zakharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1955, 224.*

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* Original Russian pagination. See C.B. Translation.

[4] R. Kh. Freidlina, E. I. Vasilyeva, Proc. Acad. Sci. USSR, 100, 85 (1955).

[5] R. Kh. Feidlina and E. I. Vasilyeva, Author's Certificate No. 105135 (USSR) (1957).

[6] Amer. Pat 2674607; Referat Zhur. Khim. 1955, 12638.

[7] E. I. Vasilyeva, and R. Kh. Feidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 177.*

[8] E. B. Trostyanskaya, I. P. Losev and A. S. Tevlina, Progr. Chem. 24, 73 (1955).

[9] A. A. Strepikheev, V. N. Topchibasheva and T. I. Shtein, Text. Ind. No. 1, 33 (1955).

[10] A. N. Nesmeyanov, A. A. Strepicheyev, R. Ch. Freidlina, L. I. Sacharkin, E. I. Vasilyeva, G. B. Owakimyan, A. A. Beer, R. G. Petrova, Sch. A Karapetyan, W. N. Toptchibascheva, T. I. Schein, M. A. Besprosvanni, Chem. Technik, 9, No. 3, 139 (1957); A. N. Nesmeyanov, R. Kh. Feidlina, L. I. Zakharkin, E. I. Vasilyeva, R. G. Petrova, Sh. A Karapetyan, G. B. Ovakimyan, A. A. Beer and M. A. Besprozvanny, The Chemical Treatment of Petroleum Hydrocarbons. (Acad. Sci. USSR Press, 1956), 302.**

[11] R. Kh. Feidlina, L. I. Zakharkin, Author's Certificate 100341 (USSR) (1955).

[12] A. N. Nesmeyanov, L. I. Zarkharkin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1953, 988.*

[13] C. Schotten, Ber. 21, 2240 (1888).

[14] D. D. Coffman, N. Z. Cox, E. L. Martin, W. E. Mochel, and F. J. Van Natta, J. Polymer. Sci. 3, 85, (1948).

[15] R. Takamoto, J. Pharm. Soc. Japan, 48, 872 (1928); Ch. A. 23, 1617 (1929).

[16] A. N. Nesmeyanov, L. I. Zakharkin, R. Kh. Feidlina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 34.*

[17] Y. Asahina, and M. Akasu, J. Pharm. Soc. Japan, 523, 479 (1925); Ch. A. 20, 365 (1926).

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* Original Russian pagination. See. C.B. Translation.

** In Russian.

# INVESTIGATION OF HYDROXYDIHYDROFURANS

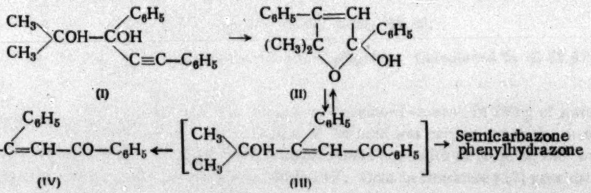
## VI. THE REACTION OF 5,5-DIMETHYL-2,4-DIPHENYL-2-HYDROXY-2,5-DIHYDROFURAN WITH 2,4-DINITROPHENYLHYDRAZINE

E. D. Venus-Danilova, L. A. Pavlova and A. Fabritsy

From literature it is known that acetylene α-glycol — unsymm. dimethyl-phenyl-phenylacetylenyl-ethylene glycol (2-methyl-3,5-diphenyl-4-pentin-2,3-diol) (I) — is, when heated with acids, converted to the isomeric 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran (II) [1-3], which can change to the tautomeric form — ethylene γ-keto-alcohol — 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one (III). The fact that a semicarbazone and a phenylhydrazone are obtained from hydroxydihydrofuran in the presence of a few drops of concentrated acetic acid and that the product of the dehydration of the ethylene γ-keto-alcohol (III) — 2-methyl-3,5-diphenyl-1,3-pentadiene-5-one (IV) [4] — can be isolated from the acid reaction mixture obtained by the isomerization of unsymm. dimethyl-phenyl-phenylacetylenyl-ethylene glycol (I) is proof of the formation of the ethylene γ-keto-alcohol.

It was not possible to isolate the corresponding ethylene γ-ketc-alcohol of the above-mentioned hydroxydihydrofuran but by the action of sulfuric acid on unsymm. dimethyl-phenyl-tertiary butylacetylenyl-ethylene glycol [5] both tautomeric forms were isolated and their mutual conversions were proven.

As was recently shown by A. Fabritsy [3, 6], by the action of various mercury salts on 2-methyl-3,5-diphenyl-4-pentin-2,3-diol (I) a mixture of mercury-containing products, free hydroxydihydrofuran (II) and its complexes with mercury salts are obtained. Since it was difficult to isolate pure hydroxydihydrofuran from these mixtures the idea arose of isolating or detecting hydroxydihydrofuran in the form of a carboxylic derivative, taking advantage of the fact that in an acid medium hydroxydihydrofuran can react like an unsaturated γ-keto-alcohol [2].



We decided on 2,4-dinitrophenylhydrazine as the most active reagent for the carboxylic group since semicarbazide and phenylhydrazine give the corresponding derivatives only with pure hydroxydihydrofuran and show only a very weak reaction to it in mixtures.

When experiments were conducted to obtain a 2,4-dinitrophenylhydrazone from 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran it was found that different products of the reaction of hydroxydihydrofuran (II) with 2,4-dinitrophenylhydrazine are obtained, depending on the experimental conditions.

For example, when an alcoholic solution of 2,4-dinitrophenylhydrazine, containing sulfuric acid, was allowed to act on an alcoholic solution of hydroxydihydrofuran a bright-yellow substance which filled the whole volume of the liquid was formed at once. When washed with water or aqueous alcohol the yellow needles were converted into an orange powder and a considerable amount of sulfuric acid was found in the wash water. The orange powder was converted into the bright-yellow substance again by the action of an alcoholic-aqueous solution of sulfuric acid. A full ultimate analysis of the orange substance showed that it had the empirical formula $C_{30}H_{28}O_9N_8$ (VI), i.e., it contained two 2,4-dinitrophenylhydrazine groups per molecule of initial substance and was evidently the 2,4-dinitrophenylhydrazino-hydrazone of the ethylene γ-keto-alcohol (III). From the analytical data the bright-yellow substance corresponded to the salt of this hydrazino-hydrazone, containing two molecules of sulfuric acid per molecule of hydrazino-hydrazone

$$C_{30}H_{28}O_9N_8 \cdot 2H_2SO_4, \ (C_{30}H_{32}O_{17}N_8S_2) \ (V, \ V\text{-a}).$$

To avoid the formation of 2,4-dinitrophenylhydrazino-hydrazone sulfate, experiments on the reaction of hydroxydihydrofuran (II) with 2,4-dinitrophenylhydrazine were carried out in an alcoholic medium in the presence of a small quantity of hydrochloric and acetic acids.

In the first instance a dark-yellow dense crystalline precipitate was rapidly formed; this had the empirical formula $C_{24}H_{22}O_5N_4$ (VII), i.e., the product contained one 2,4-dinitrophenylhydrazine group per molecule of initial hydroxydihydrofuran.

When an excess of a saturated solution of 2,4-dinitrophenylhyrazine in 75 % acetic acid was allowed to act on an alcoholic solution or an acetic-acid solution of hydroxydihydrofuran, fine yellow lustrous crystals having, like substance (VI), the empirical formula $C_{30}H_{28}O_9N_8$ were precipitated within a day. This product had different properties, however, from product (VI), obtained by the hydrolysis of 2,4-dinitrophenylhydrazino-hydrazone sulfate (V).

On the basis of a number of experiments it was established that the products of the reaction of hydroxydihydrofuran (II) with 2,4-dinitrophenylhydrazine are partially mutually convertible. For example, the yellow 2,4-dinitrophenylhydrazino-hydrazone (VIII) obtained in the presence of acetic acid is converted on boiling with glacial acetic acid into the dark-yellow 2,4-dinitrophenylhydrazone (VII), splitting off 2,4-dinitrophenylhydrazine and when acted on by an alcoholic solution of sulfuric acid forms the bright-yellow salt of 2,4-dinitrophenylhydrazino-hydrazone (V, Va). This same salt is obtained by heating the 2,4-dinitrophenylhydrazone (VII) with an alcoholic solution of 2,4-dinitrophenylhydrazine sulfate.

When recrystallized from glacial acetic acid or ethyl alcohol the orange 2,4-dinitrophenylhydrazino-hydrazone (VI) splits off 2,4-dinitrophenylhydrazine and forms the 2,4-dinitrophenylhydrazone (VII).

As regards the structure of the substances obtained it may be considered as established that the dark-yellow product containing one 2,4-dinitrophenylhydrazine group has the structure of the normal 2,4-dinitrophenylhydrazone (VII) and not that of the isomeric pyrazoline. The substance does not give Knorr's characteristic color reaction for pyrazoline [7] and when reduced with stannous chloride in the presence of hydrochloric acid gives 1,2,4-triaminobenzene. The conversion to the hydrazino-hydrazone sulfate when boiled with an alcoholic solution of the 2,4-dinitrophenylhydrazine sulfate confirms the normal structure of the hydrazone. In this process product (VII) is evidently hydrolyzed to the ethylene γ-keto-alcohol and the 2,4-dinitrophenylhydrazino-hydrazone sulfate, which is usually obtained under these conditions, is then formed. This structure of the product is also confirmed by data in literature. It is known that p-nitro- and 2,4-dinitrophenylhydrazones of unsaturated ketones are not converted into pyrazolines [8].

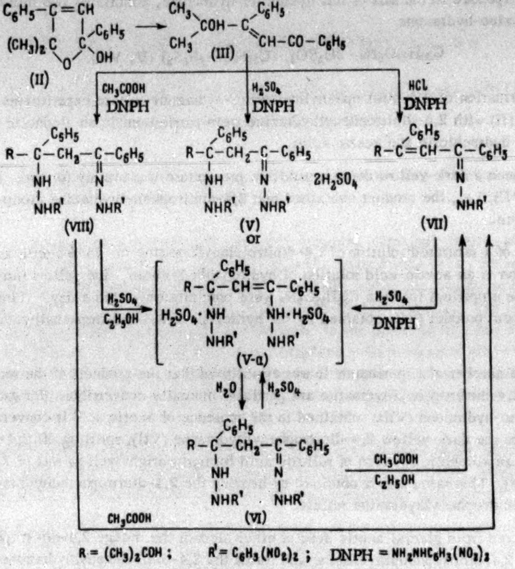
The yellow substance (VIII) obtained from hydroxydihydrofuran in a medium of acetic acid and the orange substance (VI) — the hydrolysis product of the sulfate — are two isomeric 2,4-dinitrophenylhydrazino-hydrazones. As a result of the interaction of the tautomeric forms both substances form hydroxydihydrofuran (II) with two molecules of 2,4-dinitrophenylhydrazine, one molecule of 2,4-dinitrophenylhydrazine being added at the double bond and the other reacting with the carboxylic group. It was not possible to obtain direct conversions of these substances. The yellow and the orange product evidently have a different stereochemical structure.

From literature it is known that α, β-unsaturated ketones can add reagents at the double-bond carbonyl group: for example, the addition of semicarbazide [9], hydroxylamine and methoxyhydroxylamine [10], and phenylhydrazine [11] at the multiple bonds of ethylene and acetylene ketones.

It was shown above that from analytical data the 2,4-dinitrophenylhydrazino-hydrazone sulfate contains two molecules of sulfuric acid.

It may be assumed that hydrazino-hydrazones form a salt in the tautomeric form (Va), in which there are two identical salt-forming groups.

All the substances we obtained are shown together with their mutual conversions in the system below.



$R = (CH_3)_2COH$ ; $R' = C_6H_3(NO_2)_2$ ; DNPH $= NH_2NHC_6H_3(NO_2)_2$

## EXPERIMENTAL

### 1. The Reaction of 5,5-Dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran with 2,4-Dinitrophenylhydrazine in the Presence of Sulfuric Acid.

1st Experiment. A solution of 0.4 g of 2,4-dinitrophenylhydrazine, 2 ml of sulfuric acid (d 1.84), 3 ml of water and 10 ml of ethyl alcohol was added to a solution of 0.4 g of hydroxydihydrofuran (m.p. 101°) in 10 ml of ethyl alcohol [12]. After 1-2 minutes spherical clusters of fine yellow crystals began to appear in the transparent yellow solution and after 5 minutes the entire contents of the flask solidified into a pale-yellow dense mass. After 2 hours the substance obtained was filtered and washed with dilute alcohol and then with water. As a result the bright-yellow precipitate was reduced in volume, made darker and converted into an orange product. The washing of the precipitate was continued until the wash water gave a negative reaction for the $SO_4''$ ion; this required a considerable time and the use of a large amount of water. After drying in a vacuum desiccator over calcium chloride the orange substance obtained had an m.p. of 156-157° (decomp.).

Found %: C 55.54; H 4.69; N 17.49. $C_{30}H_{28}O_9N_8$. Calculated %: C 55.90; H 4.35; N 17.39.

From the analytical data it may be assumed that the orange substance obtained was the 2,4-dinitrophenylhydrazino-hydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one (VI).

By the action of water or, better, alcoholic-aqueous sulfuric acid on this substance it was converted into the initial bright-yellow substance. When the orange product (temp. decomp. 156-157°) was recrystallized from ethyl alcohol with the addition of a small amount of ethyl acetate fine dark-yellow cubes with an m.p. of 167-168° (decomp.) were precipitated and an orange-brown substance with an m.p. of 188-191° (decomp.) settled out on the walls of the beaker; in a mixed melt with 2,4-dinitrophenylhydrazine this substance showed no depression of the melting point. In a mixture with the orange substance (VI) the dark-yellow crystals with an m.p. of 167-168° (decomp.) had an m.p. of 148-151°.

Found %: C 64.51, 64.48; H 5.28, 5.17; N 12.90, 13.00. $C_{24}H_{22}O_5N_4$. Calculated %: C 64.57; H 4.93; N 12.56.

From the analytical data the substance with an m.p. of 167-168° (decomp.) corresponded to the 2,4-dinitrophenylhydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one (VII).

A similar product was obtained by recrystallizing the orange substance from glacial acetic acid. The product had an m.p. of 167-168°, it showed no depression of the melting point in a mixed melt with the 2,4-dinitrophenylhydrazone (VII) but showed a marked depression with the initial substance.

Found %: N 12.72. $C_{24}H_{22}O_5N_4$. Calculated %: N 12.56.

2nd Experiment. The amounts of the initial substances and the experimental conditions were similar to experiment 1 except that the bright-yellow product was washed several times with anhydrous alcohol and then with absolute ether. After drying over calcium chloride in a vacuum desiccator the bright-yellow substance melted at 178-179° (decomp.).

Found %: C 42.98, 42.71; H 4.15, 4.12; N 13.51, 13.07; S 7.54, 7.86. $C_{30}H_{32}O_{17}N_8S_2$. Calculated %: C 42.85; H 3.80; N 13.33; S 7.62.

The analytical results obtained showed that the bright-yellow substance which was formed by the reaction of hydroxydihydrofuran with 2,4-dinitrophenylhydrazine in an alcoholic medium in the presence of sulfuric acid was the sulfate of 2-methyl-3,5-dinitrophenyl-3-penten-2-ol-5-one-2,4-dinitrophenylhydrazino-hydrazone (Va).

A number of experiments were carried out on the reaction of hydroxydihydrofuran with 2,4-dinitrophenylhydrazine, the concentration of the solution of the initial hydroxydihydrofuran and the ratio of the reacting substances being varied; in every case only the above-described salt was obtained.

### 2. The Reaction of 5,5-Dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran with 2,4-Dinitrophenylhydrazine in the Presence of Hydrochloric Acid [13]

A solution of 2.5 g of 2,4-dinitrophenylhydrazine in 125 ml of alcohol and 2.5 ml of hydrochloric acid (d 1.19) previously heated to boiling and filtered during cooling was added to 2.5 g of hydroxydihydrofuran in 50 ml of 96 % ethyl alcohol. After both solutions had been mixed for about 20 minutes the first small crystals appeared and a dark-yellow precipitate was rapidly formed, part of which was dried in air and part washed with water until the wash water gave a negative reaction for the chlorine ion. In both instances the substance melted at 167° (decomp.). After we recrystallized the substance from alcohol and glacial acetic acid no change in the melting point was found. A mixed melt with the 2,4-dinitrophenylhydrazone (VII) obtained by recrystallizing the orange product (VI) showed no depression of the melting point. Both substances had identical absorption curves in the ultraviolet region (see Fig. 1).

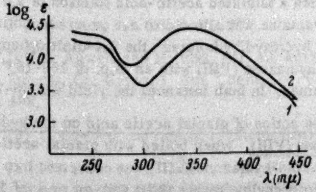


Fig. 1. Absorption spectrum in ethyl alcohol.
1) 2,4-dinitrophenylhydrazone (VII).
2) 2,4-dinitrophenylhydrazino-hydrazone (VIII).

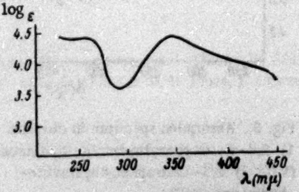


Fig. 2. Absorption spectrum of the hydrogen sulfate of the 2,4-dinitrophenylhydrazino-hydrazone (Va) in ethyl alcohol.

The yield was 3.2 g (76 %), assuming the substance to be the 2,4-dinitrophenylhydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one (VII).

Found %: C 64.47, 64.42; H 5.13, 5.24; N 12.69. $C_{24}H_{22}O_5N_4$. Calculated %: C 64.57; H 4.93; N 12.56.

The action of 2,4-dinitrophenylhydrazine on the 2,4-dinitrophenylhydrazone (VII). A small amount of the hydrazone was dissolved in alcohol with heating, a solution of 2,4-dinitrophenylhydrazine prepared in the usual manner [12] was added and the mixture heated for several minutes to boiling. On cooling, a bright-yellow flocculent precipitate was formed which had an m.p. of 174-177°, showed no depression of the melting point in a mixed melt with the salt of the 2,4-dinitrophenylhydrazino-hydrazone (Va) and had the same absorption curve in the ultraviolet region as product (Va) (see Fig. 2).

Found %: C 40.65; H 4.10; N 12.86. $C_{30}H_{28}O_9N_8 \cdot 2H_2SO_4$. Calculated %: C 42.85; H 3.80; N 13.33.

Reduction of the 2,4-dinitrophenylhydrazone (VII). When 1.5 g of the 2,4-dinitrophenylhydrazone, 8 g of $SnCl_2 \cdot 2H_2O$, 25 ml of hydrochloric acid (d 1.19) and 25 ml of water were mixed, spontaneous evolution of heat occurred. The mixture was heated to boiling with stirring for 2 hours and left for a day. The yellowish-gray precipitate formed was filtered and washed with water. The filtrate and the wash water were diluted to 150 ml and the tin from the solution was precipitated by electrolysis, after which the filtrate was evaporated under vacuum. A precipitate (about 0.8 g) was deposited in the form of small pale-gray needles from the concentrated solution. The substance obtained was identified as the hydrochloride of 1,2,4-triaminobenzene by color reactions with ammonia, caustic soda and ferric chloride [14] and the formation of the corresponding substituted quinoxaline by condensing with benzyl [15].

The precipitate formed by reduction had an m.p. of 230-232° (it contained tin and chlorine); it was not investigated more closely.

### 3. The Reaction of 5,5-Dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran with 2,4-Dinitrophenylhydrazone in an Acetic-acid Medium

A finely-crystalline yellow precipitate was fomed after one day from a mixture of 0.9 g of hydroxydihydrofuran dissolved in 40 ml of 80 % acetic acid and 45 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 75 % acetic acid (disregarding the amount of 2,4-dinitrophenylhydrazine); after drying over alkali in a vacuum desiccator this precipitate had an m.p. of 162-163° (with decomp.). In a mixed melt with the sulfate of the 2,4-dinitrophenylhydrazino-hydrazone (Va), with the 2,4-dinitrophenylhydrazone (VII) and also with the orange hydrazino-hydrazone (VI) a depression of the melting point was found.

Found %: C 55.74, 55.51; H 4.47, 4.64; N 17.69, 17.75. $C_{30}H_{28}O_9N_8$. Calculated %: C 55.90; H 4.35; N 17.39.

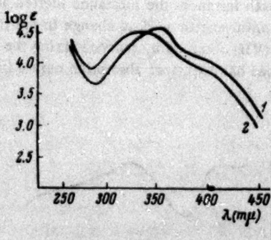


Fig. 3. Absorption spectrum in dioxane. 1) 2,4-dinitrophenylhydrazino-hydrazone (VI). 2) 2,4-dinitrophenylhydrazino-hydrazone (VIII).

From analytical data the substance with an m.p. of 162-163° (decomp.) corresponded to the 2,4-dinitrophenylhydrazino-hydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one (VIII), isomeric with the previously obtained orange substance with an m.p. of 156-157° (decomp.) (VI). These products had different absorption spectra (Fig. 3).

When a saturated acetic-acid solution of 2,4-dinitrophenylhydrazine was allowed to act on an alcoholic solution of hydroxydihydrofuran the 2,4-dinitrophenylhydrazino-hydrazone (VIII) with an m.p. of 162-163° was also obtained. In both instances the yield was 68-76 %.

The action of glacial acetic acid on the hydrazino-hydrazone (VIII). When boiled with glacial acetic acid the hydrazino-hydrazone (VIII) was converted into the 2,4-dinitrophenylhydrazone (VII) with an m.p. of 166-167° (mixed melt, absorption curve in the ultraviolet region).

Found %: C 64.78; H 5.05; N 13.00. $C_{24}H_{22}O_5N_4$. Calculated %: C 64.57; H 4.93; N 12.56.

The action of an alcoholic solution of sulfuric acid on the hydrazino-hydrazone (VIII). 0.25 g of the hydrazino-hydrazone was dissolved in 15 ml of alcohol; 3 ml of water and 2 ml of sulfuric acid were added to the solution. The mixture was heated slightly for 3 minutes to dissolve the hydrazino-hydrazone, filtered and allowed to stand overnight.

The next day the flocculent bright-yellow precipitate which had formed was washed twice with anhydrous alcohol and absolute ether. The m.p. was 178-179° (decomp.). It showed no depression of the melting point in a mixed melt with the sulfate of the 2,4-dinitrophenylhydrazino-hydrazone. The absorption curves in the ultraviolet region of both substances coincided.

Found %: C 42.78; 43.04; H 4.17, 4.15; N 13.20. $C_{30}H_{28}O_9N_8 \cdot 2H_2SO_4$. Calculated %: C 42.85; H 3.80; N 13.33.*

In consequence, the action of sulfuric acid on an alcoholic solution of the hydrazino-hydrazone (VIII) gave the sulfate (Va). This salt was converted by hydrolysis into the orange hydrazino-hydrazone (VI).

Fig. 1 gives the absorption spectra in ethyl alcohol of the 2,4-dinitrophenylhydrazone (VII), $\lambda_{max}$ 348 mμ, ε 15900 and the 2,4-dinitrophenylhydrazino-hydrazone (obtained in the presence of acetic acid) of (VIII), $\lambda_{max}$ 338 mμ, ε 29650. Fig. 2 gives the absorption spectrum of the hydrogen sulfate of the 2,4-dinitrophenylhydrazino-hydrazone (V, Va) in ethyl alcohol, $\lambda_{max}$ 352 mμ, ε 27700. Fig. 3. shows the absorption spectra of the 2,4-dinitrophenylhydrazino-hydrazones of the yellow (VIII), $\lambda_{max}$ 345 mμ, ε 33200 and the orange (VI), $\lambda_{max}$ 355 mμ, ε 35100 in a solution of dioxane.**

## SUMMARY

1. The reaction of 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran with 2,4-dinitrophenylhydrazine under various conditions was investigated.

2. It was established that by the action of an alcoholic solution of 2,4-dinitrophenylhydrazine in the presence of sulfuric acid the sulfate of the 2,4-dinitrophenylhydrazino-hydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one is obtained; by the action of an acetic-acid solution of 2,4-dinitrophenylhydrazine the 2,4-dinitrophenylhydrazino-hydrazone of the same γ-keto-alcohol is formed while if the reaction is carried out in the presence of hydrochloric acid the 2,4-dinitrophenylhydrazone of 2-methyl-3,5-diphenyl-3-penten-2-ol-5-one is obtained.

3. It was shown that the substances obtained are capable of partial mutual conversions.

## LITERATURE CITED

[1] A. E. Favorsky and E. D. Venus, J. Russ. Phys. - Chem. Soc. 47, 133 (1915).

[2] E. D. Venus-Danilova, J. Gen. Chem. 13, 93 (1943).

[3] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1609 (1956).***

[4] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 892 (1956).***

[5] E. D. Venus-Danilova and E. P. Brichko, J. Gen. Chem. 17, 1549 (1947).

[6] E. D. Venus-Danilova and A. Fabritsy, J. Gen. Chem. 26, 1901 (1956).***

[7] L. Knorr, Ber. 26, 100 (1893).

[8] K. Auwers and H. Voss, Ber. 42, 4412 (1909); L. I. Braddock and others, Anal. Chem. 25, 301 (1953); G. D. Roberts, Ch. Green, J. Am. Chem. Soc. 68, 214 (1946); E. A. Braude, and E. R. H. Jones, J. Chem. Soc. 1945, 498.

[9] E. Bowden and others, J. Chem. Soc. 1946, 39.

[10] K. Auwers, H. Müller, J. pr. Ch. 137, 16 (1933); C. Harries, Lieb. Ann. 330, 185 (1904); A. H. Blatt J. Am. Chem. Soc. 61, 3494 (1939).

[11] E. D. Venus-Danilova and S. N. Danilov, J. Gen. Chem. 2, 644 (1932).

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* All the analyses in this work were carried out by I. A. Maretina to whom we wish to express our thanks.

** The spectra were determined on an SF-4 spectrophotometer.

*** Original Russian pagination. See C.B. Translation.

[12] R. Schreiner and R. Fuson, The Systematic Analysis of Organic Compounds [Russian Translation] (Foreign Lit. Press, 1950), p. 173.

[13] E. H. Huntress, and H. C. Walter, J. Am. Chem. Soc. 70, 3702 (1948).

[14] A. Brunner. The Analyis of Azo Dyes [in Russian] (State Chem. Tech. Press, 1933), p. 65.

[15] Beilst., IV Aufl., XXV, 375; K. Bertels, Ber. 37, 2277 (1904).

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# THE CATALYTIC PREPARATION OF KETONES FROM A MIXTURE OF ACETIC ACID AND N-BUTYL ALCOHOL

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The preparation of ketones (including mixed types) by passing acetic acid and other carboxylic acids, or their derivatives, over various catalysts was developed by Sabatier and his co-workers in 1905-1914 [1]. Fairly recently, Mazurek investigated the conversion of N-butyl alcohol into dipropylketone over mixed chrome catalysts, in particular over a Cr-Mn catalyst [2].

The catalytic conversion of mixed carboxylic acids and primary alcohols has not been ivestigated hitherto. When Yakovlev passed a mixture of acetic acid and N-butyl alcohol over the above-mentioned Mazurek Cr-Mn catalyst he obtained, in addition to acetone, a product which was apparently "35% methyl-sec.butyl-ketone with traces of methylbutylketone" [3]. The investigation we carried out showed the incorrectness of Yakovlev's experimental data and the fallaciousness of the mechanism he advanced for the formation of ketones from a mixture of acid and alcohol.

Together with the establishement ofoptimum conditions for obtaining ketones we made it our object to study the method of formation of a mixed ketone. Since the Cr-Mn catalyst is less active than copper catalysts hardly any side reactions or secondary reactions occur, with the result that the study of the reaction mechanism is facilitated.

The experiments with a mixture of acetic acid and N-butyl alcohol were carrried out in the presence of added hydrogen, the latter being in a molecular ratio of 1 : 1 to the mixture. The conditions and results of the experiments are given in Tables 1-4.

As may be seen from the data in Table 1, the most favorable temperature for the yield of mixed ketone — methylpropylketone — was 440°; this is obvious from the experiments with a mixture of acid and alcohol in a molar ratio of 1 : 1, carried out with uniform rate of feed (volumetric rate 65). The absence of esters at temperatures above 420° is probably explained by the decomposition of the butyl acetate into acetaldehyde and butyraldehyde.

The maximum yields of methylpropylketone were obtained with a 3 : 1 molar ratio of acetic acid and N-butyl alcohol (Table 2). With a further increase in the acetic acid content in the mixture to 5 moles to 1 mole of alcohol the yield of methylpropylketone was reduced. These experiments were carried out at 420° and a volumetric rate of 80.

The increase of the volumetric rate from 100 to 160 led to a negligible reduction in the yield of methylpropylketone (Table 3), as may be seen from the experiments with a mixture of acid and alcohol (1 : 1 moles) at 440°. A further increase in the volumetric rate to 200 reduced the yield of methylpropylketone to one third. With a reduction in the contact time the amounts of esters and butyraldehyde formed increased and the acetaldehyde content fell. The contact time was evidently insufficient to allow further conversions to take place, i.e. the decomposition of the butyl acetate to form acetaldehyde with subsequent condensation of the latter with butyraldehyde or acetone.

In the absence of hydrogen there was a considerable reduction in the yield of dipropylketone and the fall in the yield of methylpropylketone was less marked. The experiment without a simultaneous feed of hydrogen was carried out at 440° and a volumetric rate of 60 (Table 4). The increase in the yield of acetone may be explained

TABLE 1

| Temperature of experiments | Yields (as % of the initial mixture) | | | | | |
|---|---|---|---|---|---|---|
| | Acetone | Methylpropylketone | Dipropylketone | Esters | Butyraldehyde | Unchanged N-butyl alcohol |
| 380° | 13.4 | 11.0 | 11.1 | 6.8 | 1.8 | 21.9 |
| 400 | 6.7 | 16.4 | 17.7 | 3.5 | 1.7 | 9.0 |
| 420 | 4.9 | 18.3 | 20.3 | 0.0 | 1.3 | 2.5 |
| 440 | 5.9 | 19.3 | 20.8 | 0.0 | 1.7 | 1.9 |
| 460 | 4.1 | 19.0 | 20.0 | 0.0 | 1.8 | 0.0 |
| 480 | 3.4 | 16.8 | 14.7 | 0.0 | 1.9 | 4.3 |
| 500 | 6.1 | 14.7 | 5.7 | 0.0 | 5.3 | 15.9 |

TABLE 2

| Molar ratio of acetic acid and N-butyl alcohol in mixture | Yield (as % of the initial mixture) | | | | | |
|---|---|---|---|---|---|---|
| | Acetone | Methylpropylketone | Dipropylketone | Esters | Acetaldehyde | Butyraldehyde |
| N-Butyl alcohol | — | — | 37.2 | 4.6 | — | 2.0 |
| 1 : 2 | 4.2 | 12.3 | 27.7 | 4.0 | 3.4 | 1.2 |
| 1 : 1 | 8.4 | 13.5 | 14.0 | 0.0 | 6.4 | 1.4 |
| 2 : 1 | 11.1 | 15.6 | 10.2 | 0.0 | 9.6 | 1.6 |
| 3 : 1 | 16.5 | 18.6 | 6.4 | 1.5 | 4.3 | 0.0 |
| 5 : 1 | 20.1 | 15.0 | 4.5 | 1.3 | 2.0 | 0.0 |
| Acetic acid | 32.6 | — | — | 1.0 | — | — |

TABLE 3

| Volumetric rate | Yields ( as % of the initial mixture) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Acetone | Methylpropylketone | Dipropylketone | Esters | Acetaldehyde | Butyraldehyde | Unchanged N-butyl alcohol |
| 30 | 4.4 | 21.5 | 16.1 | 0.0 | 7.4 | 0.0 | 0.0 |
| 60 | 6.5 | 19.3 | 20.8 | 0.0 | 6.4 | 0.0 | 0.6 |
| 100 | 11.8 | 15.5 | 19.7 | 0.0 | 4.5 | 1.2 | 7.3 |
| 160 | 11.6 | 13.0 | 17.6 | 1.6 | 1.0 | 1.1 | 8.1 |
| 200 | 9.6 | 4.6 | 9.9 | 3.8 | 0.0 | 8.6 | 23.2 |

TABLE 4

| Experimental conditions | Yields (as % of the initial mixture) | | | | |
|---|---|---|---|---|---|
| | Acetone | Methylpropylketone | Dipropylketone | Acetaldehyde | Butyraldehyde |
| Mixture of acetic acid and N-butyl alcohol | | | | | |
| a) In the presence of hydrogen . . . . . | 5.9 | 19.3 | 20.8 | — | 1.7 |
| b) Without hydrogen . . . . . . . . . . . . | 14.8 | 14.8 | 3.7 | — | — |
| Mixture of acetaldehyde and butyraldehyde . . . . . . . . . . . . . . . . . | 1.0 | 15.8 | 13.0 | 5.6 | 1.8 |
| Mixture of acetaldehyde and acetone. . . | 42.1 | 5.2 | — | 6.0 | — |

by the fact that the ketonic decomposition of acetic acid on oxide catalysts does not require the additional introduction of hydrogen. The addition of hydrogen has a favorable influence on the reaction of the formation of dipropylketone.

Additional experiments with mixtures of acetaldehyde and butyraldehyde and acetaldehyde and acetone (both mixtures having a 1 : 1 mole ratio) were carried out at 440°, a volumetric ratio of 60 and a simultaneous feed of hydrogen in a molar ratio of 1 : 1, in order to explain the methods of formation of methylpropylketone. From a comparison of the results of these experiments (Table 4) it may be concluded that a mixture of acetaldehyde and butyraldehyde is very readily converted into a mixture of ketones (methylpropylketone, acetone). A mixture of acetaldehyde and acetone is less reactive and gives a considerably smaller yield of methylpropylketone. The formation of methylpropylketone may, therefore, be explained by the aldol condensation of acetaldehyde with butyraldehyde (or with acetone).

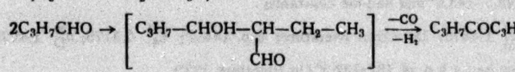
The systems for the successive conversion of a mixture of acetic acid and N-butyl alcohol are given below.

1. Formation of acetone

$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O.$$

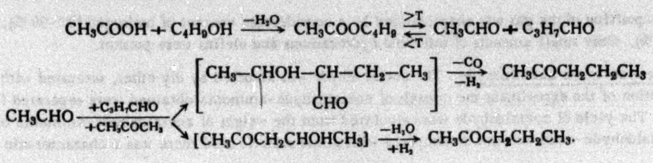
2. Formation of dipropylketone

$$2C_4H_9OH \longrightarrow H_2 + 2C_3H_7CHO$$



$$2C_3H_7CHO \rightarrow \left[ C_3H_7{-}CHOH{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}CH_2{-}CH_3 \right] \xrightarrow[-H_2]{-CO} C_3H_7COC_3H_7.$$

3. Formation of methylpropylketone



$$CH_3COOH + C_4H_9OH \xrightarrow{-H_2O} CH_3COOC_4H_9 \underset{<T}{\overset{>T}{\rightleftarrows}} CH_3CHO + C_3H_7CHO$$

$$CH_3CHO \xrightarrow[+CH_3COCH_3]{+C_3H_7CHO} \left[ CH_3{-}CHOH{-}\underset{\displaystyle CHO}{\underset{|}{CH}}{-}CH_2{-}CH_3 \right] \xrightarrow[-H_2]{-CO} CH_3COCH_2CH_2CH_3$$

$$[CH_3COCH_2CHOHCH_3] \xrightarrow[+H_2]{-H_2O} CH_3COCH_2CH_2CH_3.$$

## EXPERIMENTAL

Apparatus, general procedure and analysis of the reaction products described in [4]. In the experiments with mixtures of acetaldehyde and butyric aldehyde (or acetone) a glass jacket was placed on the mercury dropper to cool the initial mixture with running water in order to avoid evaporation of the acetaldehyde.

The catalyst was prepared by the prescribed method [2]; the activity of the catalyst was checked with N-butyl alcohol (the yield of dipropylketone was usually not less than 30-35 % of the alcohol passed over the catalyst).

Ketonization of a mixture of acetic acid and N-butyl alcohol. Commercial acetic acid (97.5 %), $d^{20}$ 1.056 and N-butyl alcohol, which after drying over $Na_2SO_4$ and distillation had a b.p. of 116.5-117.5°, $d^{20}$ 0.812 and $n_D^{20}$ 1.3990 were used in this work.

The liquid condensates from each experiment were fractionated in a fractionating column. When the condensates were distilled the following fractions were usually obtained: 1st, 54-60°, 2nd, 60-80°, 3rd, 80-90°, 4th, 98-103°, 5th, 105-120°, 6th, 120-140°, 7th, 140-144° and a residue.

The 1st fraction contained acetone which was separated by repeated distillation and identified:

b.p. 56-56.5°, $d_4^{20}$ 0.7918, $n_D^{20}$ 1.3590.

Data from literature: b.p. 56°, $d_4^{20}$ 0.7912, $n_D^{20}$ 1.3590.

A semicarbazone with an m.p. of 187-188° was obtained (in literature 188°).

The 2nd fraction was not more than 2-3 % of the weight of the condensate and contained butyraldehyde which was determined by Petrova and Zhezmer's method [5].

The 3rd fraction contained an azeotropic mixture of methylpropylketone with 13 % of water (data in literature gives the b.p. of the azeotropic mixture as 82.9°). The ketone content was determined by the hydroxylamine method.

The 4th fraction was almost pure methylpropylketone, which was separated by repeated distillation and identified:

b.p. 101.5-102.2°, $d_4^{20}$ 0.8075, $n_D^{20}$ 1.3900.

Data from literature: b.p. 102.3°, $d_4^{20}$ 0.80639, $n_D^{20}$ 1.39012.

The semicarbazone had an m.p. of 110-111° (in literature 112°).

The 5th fraction consisted for the most part of unchanged N-butyl alcohol. It was possible to separate the small amount of methylpropylketone contained in this fraction by repeated distillation.

The 6th fraction was not more than 2 % of the weight of the condensate and contained unreacted N-butyl alcohol and also a small amount of dipropylketone.

The 7th fraction consisted of almost pure dipropylketone. With repeated distillation the fraction passed over almost completely at 142.5-143.5° and had the constants:

$d_4^{20}$ 0.8176 and $n_D^{20}$ 1.4073. Data from literature: b.p. 144.1°; $d_4^{20}$ 0.8175; $n_D^{20}$ 1.40732.

The semicarbazone had a b.p. of 132-132.5° (in literature 133°).

The residues did not represent more than 5-7 % of the weight of the condensate and contained about 30 % of dipropylketone, according to the analyses and the data from repeated distillation.

The composition of the gas was characterized by a considerable content of hydrogen (70-80 %), $CO_2$ (11-15 %), CO (7-16 %). Only small amounts of saturated hydrocarbons and olefins were present.

*Identification of the acetaldehyde.* The acetaldehyde was absorbed by dry ether, saturated with ammonia. At the completion of the experiment the crystals of acetaldehyde-ammonia obtained were separated from the ether and weighed. The yield of acetaldehyde was calculated from the weight of acetaldehyde-ammonia obtained. When the acetaldehyde-ammonia was decomposed with dilute sulfuric acid there was a characteristic odor of acetaldehyde.

*Ketonization of a mixture of acetaldehyde and butyraldehyde.* The "Pure" grade of acetaldehyde, $n_D^{20}$ 1.3330, and butyraldehyde with $n_D^{20}$ 1.3842 were used for the preparation of the initial mixture.

When the condensate was distilled the same fractions were obtained as in the experiments with a mixture of acetic acid and N-butyl alcohol, in particular: a 56-60° fraction containing acetone; a 99-105° fraction, corresponding to methylpropylketone (94.6 % ketone, by analysis); a 139-146° fraction (by analysis, 88.6 % of dipropylketone). The distillation residue (above 150°) was 33.6 % of the weight of the condensate.

*Ketonization of a mixture of acetaldehyde and acetone.* The "Pure" grade of acetaldehyde, $n_D^{20}$ 1.3330, and acetone with a b.p. of 56.5° and $n_D^{20}$ 1.3598, were used for this work.

The following fractions were obtained by the distillation of the condensate: 1st, 56-62°, containing acetone (98.6 % of ketone, by analysis); 2nd, 81-89°, corresponding to an azeotropic mixture of methylpropylketone with water (85.2 % of ketone by analysis) and a residue with 38.1 % of ketone by analysis.

## SUMMARY

1. By passing a mixture of acetic acid and N-butyl alcohol over a Cr-Mn catalyst, methylpropylketone is formed with a yield of 20 % by weight of the initial mixture. At the same time, symmetrical ketones — dipropylketone (20 %) and acetone (6%) — are formed.

A system for the formation of methylpropylketone from a mixture of acetic acid and N-butyl alcohol was proposed.

## LITERATURE CITED

[1] P. Sabatier, Catalysis in Organic Chemistry. [Russian Translation] State Chem. Tech. Press (1932).

[2] V. V. Mazurek, Candidate's dissertation : The Catalytic Preparation of Dipropylketone from Butyl Alcohol over a Chromium Catalyst. Leningrad State University (1949).

[3] I. P. Yakovlev, J. Gen. Chem. 24, 983 (1954).*

[4] B. N. Dolgov and G. V. Golodnikov, J. Gen. Chem. 24, 987 (1954).*

[5] L. N. Petrova and V. D. Zhezmer, Factory Lab., No. 1, 38 (1951).

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* Original Russian pagination. See C.B. Translation.

# DERIVATIVES OF MONO- AND DIANHYDRIDES OF XYLITE*

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A. N. Shirshova

The chlorohydrin of 1,4-xylitane (5-chloro-1,4-anhydroxylite) and certain experiments on the synthesis of xylite dianhydride to which the structure of 1,4-2,5-dianhydroxylite was provisionally assigned were previously described [1]. We prepared new derivatives of xylite anhydrides for use in further syntheses.

Like 1,4-anhydroxylite (1,4-xylitane) the structure of xylite monoanhydride was proven by oxidation with periodic acid [2]. The synthesis in our experiments of the crystalline triphenylmethyl derivative — 5-triphenylmethyl-1,4-anhydroxylite (I) — previously described [2] in the form of the acetate, indicates the presence of one primary alcohol group in the molecule of 1,4-xylitane. This is partially confirmed by the fact that toluenesulfonic acid (tosyl) derivatives were obtained; tosyl derivatives of all three xylitane hydroxyls are obtained, however, 2,3,5-tritosyl-1,4-xylitane (III) being obtained. The triphenylmethyl ester of 1,4-xylitane was converted into 2,3-ditosyl-5-triphenylmethyl-1,4-xylitane (II). The esters, acetals and ketals of xylitane, and their derivatives, are described below.

By the action of thionyl chloride on xylitane a thionyl derivative, i.e. 3,5-thionyl-1,4-anhydroxylite (IV) was obtained instead of a chloro derivative, and from this were obtained 2-acetyl-3,5-thionyl-1,4-anhydroxylite (V), 2-benzoyl-3,5-thionyl-1,4-anhydroxylite (VI) and 2-tosyl-3,5-thionyl-1,4-anhydroxylite (VII). It was not possible to remove the sulfite group, leaving the tosyl and benzoyl groups at the second carbon atom because of the simultaneous hydrolysis of these and other groups; it was also not possible to obtain the triphenylmethyl ester of the thionyl compound, a fact which indicates the absence of a free primary alcohol group.

3,5-Methylene-1,4-xylite (VIII) was obtained in the form of the benzoate (IX) (2-benzoyl-3,5-methylene-1,4-xylitane) and the tosyl derivative (X) (2-tosyl-3,5-methylene-1,4-xylitane). Similar substances were synthesized from 3,5-benzylidene-1,4-xylitane (XI); 3,5-isopropylidene-1,4-xylitane (XIV); 3,5-cyclohexylidene-1,4-xylitane (XVII); 2-benzoyl-3,5-benzylidene-1,4-xylitane (XII); 2-tosyl-3,5-benzylidene-1,4-xylitane (XIII); 2-benzoyl-3,5-isopropylidene-1,4-xylitane (XV); 2-tosyl-3,5-isopropylidene-1,4-xylitane (XVI); 2-benzoyl-3,5-cyclohexylidene-1,4-xylitane (XVIII); 2- tosyl-3,5-cyclohexylidene-1,4-xylitane (XIX). In addition, urethanes were obtained from acetone-xylitane (XIV) and a benzaldehyde acetal (XI): 2-carbanilo-3,5-isopropylidene-1,4-xylitane (XX) and 2-carbanilo-3,5-benzylidene-1,4-xylitane (XXI).

To confirm the location of the acetal and ketal groups in the 3,5 position experiments were carried out to obtain triphenylmethyl derivatives but these attempts were, however, not successful. This indicates that there is no free primary alcohol group in the acetals and ketals of xylitane. Experiments on the oxidation of the acetals with an aqueous solution of potassium permanganate did not give positive results since the action of the oxidizing agent was feeble and the acetal and ketal groups were split off by the oxidizing action.

To determine whether the acetal and ketal groups were actually in the 3,5 position their tosyl derivatives (X, XIII, XVI, XIX) and their benzoates (IX, XII, XV, XVIII) were hydrolyzed but it was found that during hydrolysis in an acid medium the tosyl groups were also split off at the same time as the acetal and keto groups, the tosyl group increasing the stability of the acetal and ketal group. In the case of the benzoates of acetone-xylite (XV) and cyclohexanone-xylite (XVIII) it was possible, however, to split off the ketal groups by heating with aqueous acetic acid and to obtain the same 2-benzoyl-1,4-xylitane (XXII). Xylitane monobenzoate is not oxidized by lead tetraacetate, indicating the absence of two hydroxyl groups side by side in its molecule. This proves that in these two ketals of xylitane the two ketal groups are identically situated, evidently being in the 3,5 position. In the case of the benzoates of methylenexylitane (IX) and benzylidenexylitane (XII) simultaneous splitting off of the acetal and benzoyl groups occurs when heated with aqueous acetic acid.

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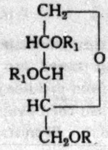
* This article is the 5th communication in the series : "Anhydrides, amino- and guanido derivatives of hydrocarbons and polyhydric alcohols." See the 4th communication in the series: J. Gen. Chem. 27, 945 (1957).

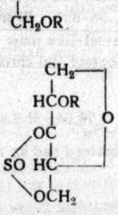
According to our experiments the best method for obtaining dianhydroxylite is the dehydrochlorination of xylitane chlorohydrin, previously described by one of the authors [1]. The following derivatives of xylitane chlorohydrin were synthesized: 2,3-carbanilo-5-chloro-1,4-anhydroxylite (XXIII), 2,3-ditosyl-5-chloro-1,4-anhydroxylite (XXIV) and the monourethane of xylitane chlorohydrin for which the position of the urethane (carbanilo) group has not yet been proven (XXV). Xylitane chlorohydrin does not form acetals and ketals, which indicates that the chlorine is located in the 5 position in 1,4-xylitane and that the acetal and ketal groups are in the 3,5 position in xylitane.

The following previously unknown derivatives of xylitane dianhydride were obtained: 3-acetyl-1,4-2,5-dianhydroxylite (XXVI), 3-benzoyl-1,4-2,5-dianhydroxylite (XXVII), 3-tosyl-1,4-2,5-dianhydroxylite (XXVIII), 3-carbanilo-1,4-2,5-dianhydroxylite (XXIX).

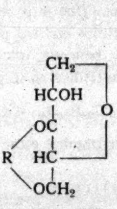
The failure of our attempts (omitted in our account of the experiments) to synthesize triphenylmethyl esters from acetals and ketals of 1,4-xylitane, and, in addition, the fact that acetals, ketals and a triphenylmethyl ester were not obtained from xylitane chlorohydrin confirm that the acetal and ketal groups in the acetals and ketals of xylitane are really located at the 3 and 5 carbon atoms and that the chlorine atom in chlorohydrin is situated in the primary alcohol group.



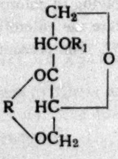
$R=C(C_6H_5)_3$;  $R_1=H$  (I)
$R=C(C_6H_5)_3$;  $R_1=SO_2(C_6H_4)CH_3$  (II)
$R$ & $R_1=SO_2(C_6H_4)CH_3$, i.e. Ts  (III)



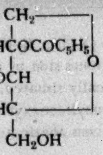
$R=H$  (IV)
$R=COCH_3$  (V)
$R=COC_6H_5$  (VI)
$R=Ts$  (VII)



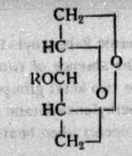
$R=CH_2$  (VIII)
$R=CHC_6H_5$  (XI)
$R=C(CH_3)_2$  (XIV)
$R=$cyclo$-C_6H_{10}$  (XVII)



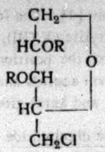
$R=CH_2$,  $R_1=COC_6H_5$  (IX),  $R_1=Ts$  (X)
$R=CHC_6H_5$,  $R_1=COC_6H_5$  (XII),  $R_1=Ts$  (XIII)
$R=C(CH_3)_2$,  $R_1=COC_6H_5$  (XV),  $R_1=Ts$  (XVI)
$R=C-C_6H_{10}$,  $R_1=COC_6H_5$  (XVIII),  $R_1=Ts$  (XIX)
$R=C(CH_3)_2$,  $R_1=CONHC_6H_5$  (XX)
$R=CHC_6H_5$,  $R_1=CONHC_6H_5$  (XXI)



(XXII)



R=COCH$_3$ (XXVI)
R=COC$_6$H$_5$ (XXVII)
R=Ts (XXVIII)
R=CONHC$_6$H$_5$ (XXIX)



Both R=CONHC$_6$H$_5$ (XXIII)
Both R=Ts (XXIV)
One R=CONHC$_6$H$_5$ (XXV)

## EXPERIMENTAL

### 1. Esters, Acetals and Ketals of Xylitane

(Investigated by A. N. Anikeeva)

### Triphenylmethyl Ester of Xylitane

A mixture of 0.5 mole of xylitane and 0.1 mole of triphenylchloromethane in equal volumes of pyridine was left for 2 days at room temperature after which the mixture was poured into water containing ice. The pale-yellow viscous oil (which crystallized after carefully washing free from pyridine) was dissolved in ether and the solution was dried with anhydrous sodium sulfate. When the ether had been evaporated in a vacuum desiccator a finely-crystalline powder remained (the m.p. was not sharp, 55-60°). Recrystallization experiments did not give good crystals with a more definite melting point; a caramel-like mass was obtained. The substance was soluble in alcohols, ether, acetone, benzene, toluene, ethyl acetate and chloroform and insoluble in water. The 5-triphenylmethyl-1-anhydroxylite (I) had an m.p. of 60°.

Found %: C 76.30; H 6.52. $C_{24}H_{24}O_4$. Calculated %: C 76.64; H 6.42.

The diacetate of this triphenylmethyl ester which we obtained had an m.p. of 134-135°.

### Ditosyl-trityl Ester of Xylitane

The ditosyl derivative of the trityl ester, 5-trityl-3,4-ditosyl -1,4-xylitane (II), was obtained. The initial triphenylmethyl ester of xylitane (0.01 mole) in a 5-fold amount of pyridine was treated with toluenesulfonyl-chloride (0.02 mole). The solution was left at room temperature for 48 hours and then poured into cold water; a viscous colorless mass separated which after washing with water and dissolving in chloroform was found to be free from pyridine. After the solution had been dried with magnesium sulfate the chloroform was driven off; the residue crystallized in the form of colorless prisms. The m.p. was 146-147°. The product was soluble in alcohol, chloroform, benzene and ether and insoluble in water.

Found %: S 9.38. $C_{38}H_{35}O_8S_2$. Calculated %: S 9.35.

### Tritosyl Ester of Xylitane

45 g of p-toluenesulfonyl chloride was added in stages to a solution of 10 g of xylitane in 100 ml of anhydrous pyridine; the mixture was left for a day at the normal temperature and then poured with stirring into ice water. The viscous mass which formed was carefully washed free from pyridine, after which it crystallized. After it had been recrystallized twice from alcohol the substance had an m.p. of 106°. 10.5 g (25 %) of the substance was obtained in the form of needles; it was soluble in acetone, benzene, ethyl acetate, chloroform, and in methyl

and ethyl alcohol with heating but insoluble in ethyl ether and water. The substance was the tritosyl ester of xylitane, 2,3,5-tritosyl-1,4-anhydroxylite (III).

Found %: C 52.42; H 4.32; S 15.99, 15.98. $C_{26}H_{28}O_{10}S_3$. Calculated %: C 52.36; H 4.69; S 16.10.

## 1,4-Xylitane Sulfite and its Derivatives (from A. N. Shirshova's experiments)

When xylitane is acted on by thionyl chloride, xylitane sulfite is formed, not xylitane chlorohydrin. Thionyl chloride was added dropwise to 100 g of freshly-distilled xylitane. It was necessary to cool the flask with ice in order to avoid the intense evolution of heat. It was left overnight and the excess thionyl chloride was then distilled under vacuum. It was kept over alkali in a desiccator for 5 days to remove traces of thionyl chloride. After distillation at 140° and 0.5 mm, 50 g of a pale-yellow liquid was obtained which completely crystallized on keeping. After it had been recrystallized several times from ether the xylitane sulfite had an m.p. of 83-84°. The substance was soluble in acetone and in alcohol and benzene when heated.

Found (mean of two analyses, as elswhere) %: C 33.30; H 4.62; S 18.00. $C_5H_8O_5S$. Calculated %: C 33.33; H 4.40; S 17.70.

The substance was, therefore, 3,5-thionyl-1,4-anhydroxylite (IV).

Acetyl derivative of xylitane sulfite. A mixture of 5 g of xylitane sulfite, 25 g of acetic anhydride and 2.5 g of anhydrous sodium acetate was heated on a boiling water bath. After the excess anhydride had been distilled the mixture was poured into water and the oil formed was dissolved in ether and the solution washed with 1 % alkali. After it had been dried with phosphorus pentoxide the substance was distilled under vacuum.

B. p. 105-107° (0.15 mm), $d_0^{20}$ 1.4261, $n_D^{20}$ 1.4810, $MR_D$ 44.10; Calc. 44.54.

Found %: C 38.28; H 4.18; S 14.37. $C_7H_{10}O_6S$. Calculated %: C 38.00; H 4.53; S 14.40.

The substance was 2-acetyl-3,5-thionyl-1,4-anhydroxylite (V).

The benzoyl derivative of 2-acetyl-3,5-thionyl-1,4-anhydroxylite (VI) was obtained by the action of benzoyl chloride in pyridine solution at room temperature for 48 hours in a sealed flask. The mixture was dissolved in chloroform, the pyridine was washed out with cooled water, 1 % hydrochloric acid, alkali and then with water again. After the solution had been dried with calcium chloride the chloroform was distilled off under vacuum. The dark-brown oil obtained crystallized and the crystals were washed with ethyl alcohol. The m.p. was 96-98°. The 2-benzoyl-3,5-thionyl-1,4-anhydroxylite was soluble in acetone, benzene and chloroform, and in alcohol and gasoline when heated.

Found %: C 50.43; H 4.33; S 11.79. $C_{12}H_{11}O_4S$. Calculated %: C 50.70; H 4.20; S 11.26.

Tosyl derivative of xylitane sulfite (VII). A mixture of xylitane sulfite (10 g) in anhydrous pyridine (50 ml) and p-toluenesulfonylchloride (11 g) was kept initially at 0° and then at room temperature. After 12 hours the mixture was poured into water; the oil which separated out crystallized when washed. The crystals were washed with cold water and dried in a vacuum dryer at 20°. The tosyl derivative was very readily soluble in acetone and in chloroform, readily soluble in hot alcohol and in ether, more difficultly soluble in benzene. After it had been recrystallized from alcohol the 2-tosyl-3,5-thionyl-1,4-anhydroxylite (VII) had an m.p. of 60-61°.

Found %: C 43.33; H 4.28; S 19.50. $C_{12}H_{14}O_7S$. Calculated %: C 43.11; H 4.10; S 19.10.

## Acetals and Ketals of Xylitane

Methylene xylitane (VIII) was obtained by heating xylitane with paraformaldehyde in the presence of concentrated hydrochloric acid. The other method, heating xylitane with 37 % formalin, gives low yields, part of the xylitane being regenerated.

0.11 mole of ground and sifted paraformaldehyde and an equal weight of concentrated hydrochloric acid were added to 0.1 mole of xylitane. The mixture was carefully stirred and heated for 3 hours in a container with a ground glass stopper on a water bath (70-75°). The following day the hydrochloric acid was removed under vacuum at 50-60° and the methylene xylitane was then distilled at 138-139° (0.5 mm) in the form of a colorless syrup which crystallized during distillation. If any unreacted paraformaldehyde remained, it was advantageous, prior to distillation, to dissolve the reaction mass in alcohol, after removing the water and hydrochloric acid under vacuum, precipitate the paraformaldehyde with ethyl ether and then remove the solvent. After recrystallizing from alcohol the methylene xylitane had an m. p. of 77°.

Found %: C 49.30; H 7.20; $C_6H_{10}O_4$. Calculated %: C 49.32; H 6.91.

The benzoyl derivative of methylene xylitane (IX) was obtained by reacting 5 g of the acetal and 5 g of benzoyl chloride in pyridine solution. The product (yield 3.7 g ) was recrystallized from ethyl alcohol; it had the appearance of silky needles with an m.p. of 113°. The substance was soluble in chloroform and acetone but insoluble in water.

Found %: C 62.37; H 5.77. $C_{13}H_{14}O_5$. Calculated %: C 62.40; H 5.68.

Tosyl ester of methylene xylitane (X) A 1.5-fold amount of p-toluenesulfonylchloride was added to a solution of methylene xylitane in ten-times that amount of anhydrous pyridine; the mixture was left for a day and then poured into water. A colorless thick oily substance separated out and crystallized when washed. After it had been recrystallized from methyl alcohol the substance was obtained (yield 73 %) in the form of needles, readily soluble in acetone, ether, chloroform, benzene, ethyl acetate and in ethyl alcohol but insoluble in water. The m.p. was 85°.

Found %: C 52.17; H 5.49; S 10.07. $C_{13}H_{16}O_6S$. Calculated %: C 51.98; H 5.33; S 10.06.

Benzylidene xylitane (XI) was earlier obtained by S. N. Danilov, K. V. Levitsky and S. I. Guren (at the Leningrad Technical Institute) by reacting xylitane with benzaldehyde in the presence of hydrochloric acid (d 1.19), the weight of the latter being equal to that of the xylitane. After it had been recrystallized from boiling water the acetal of benzaldehyde which was in the form of needles had an m.p. of 137-138° (slightly contaminated with benzoic acid). We obtained the best yield when we synthesized it by heating xylitane (0.5 mole) with benzaldehyde (0.55 mole) to 155-160° for 3 hours in a current of carbon dioxide. The crystalline substance was filtered and washed with ethyl ether. The substance was in the form of long silky needles with an m.p. of 139°. The yield was up to 60 % of the theoretical. Benzalxylitane was readily soluble in ethyl alcohol, acetone, chloroform, ethyl acetate and dioxane; it dissolved in boiling benzene and water, coming out of solution again on cooling.

Found %: C 64.74; H 6.56. $C_{12}H_{14}O_4$. Calculated %: C 64.80; H 6.30.

The benzoyl derivative of benzylidene xylitane (XII) was obtained by reacting 5 g of the acetal with 4.8 g of benzoyl chloride in 25 ml of pyridine. After 24 hours the solution was poured into cold water. After they had been washed crystals of the benzoate were recrystallized from ethyl alcohol. 6.8 g (93 %) of the product was obtained in the form of shiny plates; the m.p. was 133°. The benzoate was soluble in benzene, acetone and chloroform but insoluble in water.

Found %: C 70.33; H 5.63. $C_{19}H_{18}O_5$. Calculated %: C 69.93; H 5.56.

The p-toluene sulfonic acid (tosyl) ester of benzylidene xylitane (XIII) was obtained by adding 5 g of p--toluene sulfonyl chloride to a solution of 4 g of benzylidene xylitane in 50 ml of anhydrous pyridine cooled to 0°. The mixture was stirred for several minutes until the chlorohydrin dissolved and was left for a day at room temperature. The mixture was poured into cold water; the oil which separated out gradually crystallized. After it had been recrystallized form ethyl alcohol 4.6 g of a crystalline substance in the form of fine silky needles with an m.p. of 110° was obtained. The tosyl ester of benzylidene xylitane was readily soluble in gasoline, chloroform, dichloroethane, pyridine, acetone and ethyl ether but was insoluble in water and only dissolved in ethyl alcohol with heating.

Found %: C 60.75; H 5.37; S 8.25. $C_{19}H_{20}O_6S$. Calculated %: C 60.55; H 5.31; S 8.38.

The acetone compound of xylitane (XIV) was obtained (with a low yield) by S. N. Danilov and S. I. Guren (at the Leningrad Technological Institute) by heating a mixture of xylitane in a 10-fold amount of anhydrous acetone with 1 % sulfuric acid (d 1.84) for 3 hours (up to the boiling point of the acetone). The m.p. was 65-66°. We obtainedoptimum results by heating a mixture of 134 g (1 mole) of xylitane with a 3-fold amount by weight of acetone in the presence of 80 g of freshly-calcined copper sulfate for 20 hours (up to the boiling point of the acetone). After the acetone had been distilled the light-yellow syrup was distilled under vacuum. The b.p. was 127° (0.4 mm). The distilled substance rapidly crystallized. After it had been recrystallized froma mixture of alcohol and ether (1 : 3) the acetone-xylitane was obtained as colorless rhombiform crystals. The m.p. was 65°. The yield was 51 %. The acetone-xylitane was hygroscopic, readily soluble in water, alcohols, chloroform, ethyl acetate, dioxane, benzene and other solvents but less soluble in ethyl ether.

Found %: C 55.07; H 8.28. $C_8H_{14}O_4$. Calculated %: C 55.17; H 8.01.

The benzoate of acetone-xylitane (isopropylidene xylitane) (XV) was obtained by the action of benzoyl chloride (25 % excess) on the acetal (3 g), dissolved in 12 ml of 10 % caustic soda, the mixture being shaken in a container with a ground glass stopper. After 24 hours the benzoate was extracted with chloroform and the mixture was washed with water and dried with potash. The colorless vaseline-like mass obtained after driving off the chloroform crystallized on cooling. A solution of the substance in anhydrous hot methyl alcohol deposited crystals on cooling to -6°; these were washed with cooled methyl alcohol and had an m.p. of 79.5-80°. The benzoate of isopropylidene xylitane was readily soluble in chloroform, benzene and acetone, more difficulty soluble in alcohols and ethyl ether and insoluble in water. The yield was 53 %.

Found %: C 64.61; H 6.65. $C_{15}H_{18}O_5$. Calculated %: C 64.71; H 6.48.

The tosyl ester of acetone-xylitane (XVI) was obtained in a similar manner to the tosyl esters of methylene- and benzylidene xylitane. 1.9 g of a crystalline product was obtained from 2 g of acetone-xylitane and was recrystallized from ethyl alcohol; the m.p. was 84°. The substance was soluble in acetone, benzene, chloroform and alcohols; it was insoluble in water.

Found %: C 54.96; H 6.23; S 9.57. $C_{15}H_{20}O_6S$. Calculated %: C 54.86; H 6.09; S 9.75.

The cyclohexylidene derivative of xylitane * was obtained by reacting 30 g of xylitane with 27 g of freshly-distilled cyclohexanone in 40 g of ethyl ether (which gives better results than in a solution of dioxane) in the presence of 2 ml of concentrated sulfuric acid, the mixture being shaken for 10 hours. The liquid, which consisted of two layers, was neutralized with dry sodium bicarbonate. After the ethyl ether and excess cyclohexanone had been distilled a pale-yellow thick liquid remained; this was distilled under vacuum. Cyclohexylidene xylitane (yield 63 %) was a colorless viscous liquid with a pleasant odor.

The b.p. was 155-158° (0.5 mm), $n_D^{18}$ 1.5032.

Found %: C 61.38; H 8.67. $C_{11}H_{18}O_4$. Calculated %: C 61.68; H 8.41.

Analyses showed that it corresponded to 3,5-cyclohexylidene-1,4-anhydroxylite (XVII).

Benzoyl cyclohexylidene xylitane. 20 g of freshly-distilled cyclohexylidene xylitane was dissolved in 100 ml of anhydrous pyridine and 17 ml of benzoyl chloride added to the solution. After 48 hours the mixture was separated from the crystals of pyridine hydrochloride and poured into water containing ice. The vaseline-like mass which formed crystallized rapidly when washed. After it had been recrystallized from absolute methanol it was obtained as fine needles with an m.p. of 104-105°. The yield was 72 %. The product was readily soluble in benzene, chloroform, acetone and carbon tetrachloride, and in petroleum ether, alcohol and ethyl ether when boiled. From analyses made, the substance was 2-benzoyl-3,5-cyclohexylidene-1,4-anhydroxylite (XVIII).

Found %: C 68.37; H 6.96. $C_{18}H_{22}O_5$. Calculated %: C 68.00; H 6.92.

The tosyl ester of cyclohexylidene xylitane * was obtained as in the case of the above-described acetals (17 g of the acetal was mixed with cooling with 7.7 g of toluenesulfonyl chloride, 30 g of anhydrous pyridine, the mixture being kept for 24 hours at room temperature). When the mixture was poured into water a vaseline-like mass was formed which later crystallized. After it had been recrystallized twice from methyl alcohol the 2-tosyl-3,5-cyclohexylidene-1,4-anhydroxylite (XIX) had an m.p. of 96°. The tosyl ester dissolved in hot methyl and ethyl alcohol, in acetone and benzene but was insoluble in water.

Found %: C 58.59; H 6.58; S 8.73, 8.39. $C_{18}H_{23}O_6S$. Calculated %: C 58.82; H 6.28; S 8.69.

Urethane of 3,5-isopropylidene-1,4-xylitane. 1.5 g of acetone-xylitane was dissolvedin 2 ml of anhydrous chloroform; 1.1 g (10 % excess) of freshly-distilled phenyl isocyanate was added. The mixture was heated in a sealed ampoule on a water bath for 6 hours. After they had been cooled, the contents of the flask were poured into 100 ml of petroleum ether. When agitated in petroleum ether the oily layer thickened and acquired the consistency of a viscous mass; the latter was washed with three amounts of petroleum ether and dissolved in a small amount of ethyl ether. The solution rapidly crystallized. After it had been dried in a vacuum desiccator the 2-

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* Together with D. Gonzales.

-carbanilo-3,5-isopropylidene-1,4-xylitane (XX) had an m.p. of 107-108°.

Found %: C 60.85; H 7.41; N 4.96, 4.75. $C_{15}H_{19}O_5N$. Calculated %: C 61.43; H 7.48; N 4.77.

The urethane of benzylidene xylitane was obtained in a similar manner, in the form of a finely-crystalline powder with an m.p. of 197-198°. It was 2-carbanilo-3,5-benzylidene-1,4-xylitane (XXI).

Found %: C 66.95; H 6.04; N 4.47. $C_{19}H_{19}O_5N$. Calculated %: C 66.80; H 5.57; N 4.10.

Hydrolysis of the acetal groups. 5 g of the benzoate of isopropylidene cyclohexylidene xylitane was covered with 25 ml of 80 % acetic acid and heated for 45 minutes in a flask with a reflux condenser on a water bath. After it had been cooled, the acetic acid was distilled under vacuum and the residue extracted with chloroform; it was first washed with dilute alkali, then with water followed by drying with sodium sulfate. After the solvent had been distilled off the product was recrystallized from anhydrous ethyl alcohol. Xylitane monobenzoate was a finely crystalline powder soluble in organic solvents in the cold and in water with slight heating.

The same monobenzoate (XXII), which after recrystallizing twice from alcohol had an m.p. of 91-92°, was obtained in both instances. The analyses of the monobenzoate are given below.

Monobenzoate, obtained after removal of the acetone group in benzoyl acetone-xylitane:

Found %: C 59.95; 59.89; H 6.19, 5.97. $C_{12}H_{14}O_5$. Calculated %: C 60.40; H 5.88.

Monobenzoate, obtained after removal of the cyclohexylidene group in benzoyl cyclohexanone-xylitane.

Found %: C 60.34, 60.62; H 5.74, 5.70; $C_{12}H_{14}O_5$. Calculated %: C 60.40; H 5.88.

To eliminate the possibility that the benzoyl group might be located in the 5 position we oxidized the benzoate, obtained from the benzoate of the acetone derivative, with lead tetraacetate but in spite of the prolonged action of this oxidizing agent in glacial acetic acid at 45° (48 hours) the main mass of the substance was recovered unchanged and only a small amount of the oxidizing agent was consumed. The sample of the benzoate from the cyclohexylidene derivative of xylitane was, therefore, not oxidized by lead tetraacetate; this confirms that the benzoyl group is located at the 2 carbon atom and the acetyl groups between the 3 and 5 carbon atoms in the benzoates of the corresponding acetals.

To remove the acetyl groups, in the case of the tosyl derivatives of xylitane when the substance was heated on a boiling water bath or with 3 % hydrochloric acid (for the tosyl derivative of acetone-xylitane with an m.p. of 84°) or with aqueous acetic acid (for tosylbenzylidene xylitane with an m.p. of 110°) the product was partially hydrolyzed with the formation of xylitane or was in the main unchanged. This indicates that the tosyl group has a stabilizing influence on the acetal and ketal groups.

## 2. Chlorohydrin of Xylitane and Dianhydride of Xylite

(Investigation by N. S. Tikhomirova-Sidorova)

Since A. N. Shirshova did not succeed in obtaining considerable yields of 1,4-2,5-xylite dianhydride when heating 1,4-xylitane with aqueous and crystalline oxalic and phosphoric (concentration 89 %) acids at 120-140° this anhydride was prepared via xylitane chlorohydrin by the previously described method [1] with some modifications.

To obtain xylitane chlorohydrin a weighed sample of xylite or xylitane was treated in the presence of calcined magnesium sulfate by mixing with a strong current of hydrogen chloride on a water bath at 105° until the theoretical increase in weight had been obtained. After it had been neutralized with alkali the brown sirupy product was dried with calcined magnesium sulfate in anhydrous alcoholic solution and distilled three times under vacuum. After it had been seeded with a crystal of chlorohydrin the sirup obtained crystallized out in 1-2 days; it had an m.p. of 48-49° (from ethyl acetate).

B. p. 160-161° (2 mm), 140-141° (0.3 mm), $d_4^{20}$ 1.3722, $n_D^{20}$ 1.5030, $MR_D$ 32.85; Calc. 32.54.

To characterize the chlorohydrin its urethane and tosyl ester were obtained.

Ditosyl ester of xylitane chlorohydrin.* 10 g of xylitane chlorohydrin in 100 ml of pyridine and 31 g of p-toluenesulfonyl chloride were left at 0° for 12 hours. The precipitated pyridine hydrochloride was filtered and the pyridine was distilled under vacuum at 25-30° until its volume had been reduced to 1/3rd. A small amount of water was added to the residue. After several hours the oily layer had almost completely crystallized. More water was added. The crystalline precipitate was filtered and washed with cold methyl alcohol. After it had been recrystallized twice from methyl alcohol 16 g (31 %) of 2,3-ditosyl-5-chloro-1,4-anhydroxylite (XXIV) with an m.p. of 102° was obtained; after further recrystallizations the m.p. was 104°.

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* Together with G. E. Ustyuzhanin.

Found %: C 49.58, 49.26; H 4.75, 4.80; Cl 7.48; S 13.73. $C_{19}H_{21}O_7S_2Cl$. Calculated %: C 49.50; H 4.59; Cl 7.69; S 13.91.

Monophenylurethane of xylitane chlorohydrin (XXV). A mixture of 1 mole of the crystalline chlorohydrin and 1.15 mole of phenyl isocyanate was heated for 5 minutes in a sealed vessel on a boiling water bath and left to crystallize. After standing for some time in a desiccator the crystallized product was extracted with boiling petroleum ether (b.p. 80-100°) and was then crystallized from ethyl ether. When the colorless crystalline substance was carefully washed with ether and dried it had an m.p. of 137-138°, and by analysis corresponded to the monophenylurethane of xylite chlorohydrin.

Found %: C 53.03; H 5.16; N 5.82; Cl 13.00. $C_{12}H_{14}O_4NCl$. Calculated %: C 53.13; H 5.15; N 5.16; Cl 13.07.

The position of the carbonyl group was unknown (in the 2 or 3 position ?).

Diphenylurethane of xylitane chlorohydrin (XXIII). To synthesize the diurethane of xylitane chlorohydrin a mixture of 0.5 g of chlorohydrin (1 mole), 1.2 g of phenyl isocyanate (3 moles) and 3 ml of benzene were heated in an ampoule to 150° for 2 hours. The reaction mixture crystallized when cooled. The crystalline product obtained was washed free from benzene and excess phenyl isocyanate by boiling with ethyl ether and then with petroleum ether. The dried white powdery substance was recrystallized from alcohol. The precipitate separated out when the filtrate was diluted with water. After it had been dried over phosphorus pentoxide in a vacuum desiccator the pure substance had an m.p. of 151-152° and by analysis corresponded to the diurethane of xylitane chlorohydrin, i.e. it was 1-chloro-3,4-dicarbanilo-1,4-anhydroxylite.

Found %: C 58.21; H 5.05; N 7.41. $C_{19}H_{19}O_5N_2Cl$. Calculated %: C 58.38; H 4.86; N 7.17.

A yield of 78 % of the diurethane of chlorohydrin with the above-mentioned properties was also obtained by heating 1 mole of chlorohydrin and 3 moles of phenyl isocyanate to 120° for 5 hours in an ampoule without a solvent.

1,4-2,5-Xylite dianhydride was synthesized with a yield of 78 % by reacting xylitane chlorohydrin with sodium methylate in the cold in dioxane. The dianhydride was a transparent colorless liquid with a faint odor, readily soluble in water and organic solvents.

B. p. 120-121° (11 mm); 115-116° (6 mm); 103° (2 mm); 92° (1 mm); $d_4^{20}$ 1.2895, $n_D^{20}$ 1.4802, $MR_D$ 25.56; Calc. 25.76.

Found %: C 51.61; H 7.25; OH 15.49. $C_5H_8O_3$. Calculated %: C 51.70; H 6.90; OH 14.65.

Acetic and benzoic esters of 1,4-2,5-xylite dianhydride. To obtain the acetic ester (XXII) 5 g of the dianhydride was heated with 1.5 g of freshly-melted sodium acetate in 10 g of acetic anhydride for 12 hours on a water bath. It was poured into water, extracted with ether, washed with a solution of alkali and dried. The m.p. was 92° (4 mm), $n_D^{20}$ 1.4572.

Found %: C 53.22; H 6.74. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.63.

The benzoate of the 1,4-2,5-dianhydride (XXIII) was obtained by treating the dianhydride with benzoyl chloride in anhydrous pyridine for a day. The chloroform extract was washed with dilute hydrochloric acid, alkali and water, then dried with magnesium sulfate. The crystalline mass of the benzoate was recrystallized from alcohol; the crystals obtained were fine needles with an m.p. of 84°.

Found %: C 65.29; H 5.75. $C_{12}H_{12}O_4$. Calculated %: C 65.45; H 5.45.

The tosyl ester of the dianhydride (XXIX) was obtained by the action of excess toluenesulfonyl chloride in anhydrous pyridine. After a day the mixture was poured into cold water; the white powdery precipitate formed was carefully washed, dried under vacuum and recrystallized from ethyl alcohol; it had an m.p. of 96-97° (rhombic crystals).

Found %: C 53.99; H 5.34; S 11.87. $C_{12}H_{14}O_5S$. Calculated %: C 53.34; H 5.19; S 11.80.

Phenylurethane of the dianhydride (XXX). After a mixture of dianhydride and phenyl isocyanate had been kept at room temperature for 2 days the phenylurethane was precipitated from the mixture; it was recrystallized from ethyl alcohol. The m.p. was 114°.

Found %: C 61.71; H 5.56; N 6.22. $C_{12}H_{13}O_4N$. Calculated %: C 61.30; H 5.54; N 6.00.

## SUMMARY

1. The crystalline triphenylmethyl ester and tritosyl esters were synthesized from 1,4-xylitane.

2. Treatment of 1,4-xylitane with thionyl chloride did not result in chlorination but in the formation of its crystalline sulfite, characterized by the synthesis of the acetate, the benzoate and the tosyl ester.

3. The monomethylene, monobenzylidene, monoisopropylidene and monocyclohexylidene derivatives of 1,4-xylitane were prepared and characterized in the form of the acetates, benzoates, tosyl esters and urethanes. Evidence was obtained in favor of the fact that in the acetals, ketals and sulfite of 1,4-xylitane the acetals and ketals are in the 3,5 position.

4. The method of obtaining 1,4-xylitane chlorohydrin and 1,4-2,5-xylite dianhydride was improved and their esters and urethanes were obtained.

5. The structure assumed for the described substances was confirmed by hydrolysis of the tosyl and benzoic esters of the xylitane acetals and ketals.

## LITERATURE CITED

[1] S. N. Danilov, V. F. Kazimirova, J. Gen. Chem. 23, Coll. II, 1646 (1953).*

[2] Carson, Maclay, J. Am. Chem. Soc. 67, 1808 (1945).

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* Original Russian pagination. See C.B. Translation.

# THE POLYMERIZATION OF UNSATURATED ORGANOSILICON COMPOUNDS UNDER PRESSURE

V. V. Korshak, A. M. Polyakova, A. A. Sakharova, A. D. Petrov,
V. F. Mironov, V. G. Glukhovtsev and G. I. Nikishin

In previously published articles [1-3] the results were given of investigations on the polymerization and copolymerization of a considerable number (47) of different mono- and polyalkenylsilanes. The tendency to polymerize, with and without the application of pressure, of $\alpha$-, $\beta$-, $\gamma$-, $\delta$-, and $\epsilon$-alkenyl- and cyclopentadienylsilanes was studied. It was established that the tendency of alkenylsilanes to polymerize is determined both by the character of the double bond and its position with respect to the silicon atom. Silicoolefins with ethyl groups at the silicon atom were found to be more active in a polymerization reaction than those containing methyl groups in the same position. This fact was explained by the presence of $\delta,\delta$-conjugation in alkenylsilanes with ethyl groups at the silicon atom. Alkenylsilanes with a primary-secondary multiple bond polymerize more easily than alkenylsilanes containing a primary-tertiary or secondary-secondary bond.

In many examples it was found that the tendency of silicoolefins to polymerize decreases with the movement of the multiple bond from the $\alpha$- to the $\beta$-position with respect to the silicon atom and increases again with further removal from it. The greatest activity in a polymerization reaction is, therefore, possessed by those forms which are the least reactive with respect to the addition of $(CNS)_2$, $X_2$, HX etc. $\gamma$-, $\delta$- and $\epsilon$-alkenylsilanes polymerize with the formation of oils of different consistency, including highly-viscous types. A difference in the results of polymerization, with and without the use of pressure was shown. Finally, a number of copolymers of alkenylsilanes with methylmethacrylate and styrene were obtained and their thermomechanical properties were determined.

The present investigation is the continuation and extension of this work. We investigated the tendency of both mono- and dialkenylsilanes to polymerize under pressure under standard conditions (in the previous communication [3] mention was already made of three bis-trialkylsilylalkenes). Of the monoalkenylsilanes, we investigated alkylvinylsilanes with the general formula $R_3SiCH{=}CH_2$ where R = $CH_3$, $C_2H_5$, $C_3H_7$ and $C_4H_9$.

TABLE 1

| Formula of the silicoolefin | Pressure (in atm) | Concentration of initiator (mole %) | Polymerization products | | | |
|---|---|---|---|---|---|---|
| | | | External appearance of polymer obtained | Yield (as %) | Molecular weight (mean) | Coefficient of polymerization |
| $(CH_3)_3SiCH{=}CH_2$ . . . . . . | 6000 | 0.65 | Thick viscous colorless oil | 73 | 1173 | 12 |
| $(C_2H_5)_3SiCH{=}CH_2$ . . . . . . . | 6000 | 0.66 | The same | 47 | 2597 | 18 |
| $(C_2H_5)_3SiCH{=}CH_2$ * . . . . . . | 1 | 1.09 | The same | 9 | 1055 | 7.4 |
| $(C_3H_7)_3SiCH{=}CH_2$ . . . . . . . | 6000 | 0.66 | The same | 20 | 1969 | 11 |
| $(C_4H_9)_3SiCH{=}CH_2$ . . . . . . . | 6000 | 0.66 | The same | 47 | 3460 | 15 |
| $(C_2H_5)_3SiCH_2CH{=}CH_2$ * . . . . | 6000 | 0.66 | Colorless oil | 10 | 637 | 4 |

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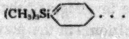
* Previously investigated under somewhat different conditions [3].

The results of the investigation, given in Table 1, confirm the laws previously established by us [3]. For example, alkylvinylsilanes polymerize far more easily than alkylallylsilanes. All the investigated alkylvinylsilanes formed very viscous oils as a result of polymerization whereas the corresponding alkylallylsilanes polymerized to form mobile oily liquids with a considerably lower polymerization coefficient than the polymers of alkylvinylsilanes. We also had an opportunity of observing the influence of various radicals on the behavior of vinylsilanes in a polymerization reaction. As would be expected, triethylvinylsilane has the maximum polymerization coefficient of the trialkylvinylsilanes. The tendency to polymerize falls with the transition to trimethylvinylsilane and tripropylvinylsilane and increases again with tributylvinylsilane. The positive influence of ethyl groups on the polymerization capacity of silicoolefins was also shown by the examples of ethyldimethylisocrotylsilane and ethyldimethylpropenylsilane (Table 2).

TABLE 2

| Formula of the silicoolefin | Pressure (in atm.) | Concentration of initiator (mole %) | Polymerization products | | | |
|---|---|---|---|---|---|---|
| | | | External appearance of polymer obtained | Yield (as %) | Molecular wt. (mean) | Polymerization coefficient |
| $(C_2H_5)(CH_3)_2SiCH=C(CH_3)_2$ . . . . | 6000 | 1 | Not polymerized | | | |
| $(C_2H_5)(CH_3)_2SiCH=CHCH_3$ . . . . | 6000 | 1 | Not polymerized | | | |
| $(CH_3)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CHCH_3$ . . . . . . . . | 6000 | 3 | Yellowish liquid | 8.5 | 317 | 2 |
| $(CH_3)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CHCH_3$ . . . . . . . . | 1 | 3 | Not polymerized | | | |
| $(CH_3)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}HCH=CHCH_3$ . . . . . . | 6000 | 1 | Not polymerized | | | |
| $(CH_3)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CHCH_2OCH_2CH_2CN$ . . | 6000 | 1 | Yellowish liquid | 6.5 | 441 | 2 |
| $(C_2H_5)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CHCH_2OCH_2CH_2CN$ . | 6000 | 1 | Not polymerized | | | |
| $(CH_3)_3Si\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CHCH_2OH$ . . . . . . | 6000 | 1 | Thick orange mass | 4.4 | 475 | 3 |
| $(C_3H_7)(CH_3)_2SiCH=CHC_6H_5$ . . . . | 6000 | 1 | Not polymerized | | | |
| $(CH_3)_3Si\underset{\displaystyle C_6H_5}{\underset{\mid}{C}}=CH_2$ . . . . . . . . . . | 6000 | 1 | Not polymerized | | | |
| $\alpha$-$C_{10}H_7Si(CH_2CH=CH_2)_3$ * . . . . | 6000 | 1 | Jelly-like mass | 15 | Trimer | |
| $\alpha$-$C_{10}H_7Si(OCH_2CH=CH_2)_3$ * . . . . | 6000 | 1 | The same | 31 | Trimer | |
|  . . . . . . . . . . | 6000 | 1 | Not polymerized | | | |

Whereas neither of these compounds takes part in the polymerization reaction, similar compounds containing $(C_2H_5)_3Si$-radicals instead of $(C_2H_5)(CH_3)_2Si$-groups, formed polymers, a tetramer and a dimer, respectively [3].

The examples of silicoolefins also demonstrated the general laws established for unsaturated compounds (substituted ethylenes). We showed (Table 2), for example, that $\beta$-(propyldimethylsilyl)-styrene cannot polymerize. The structural analog of $\alpha$-methylstyrene — $\alpha$-(trimethylsilyl)-styrene — does not polymerize according to the radical mechanism either.

The steric hindrances found in the case of $\alpha$-methylstyrene are intensified with $\alpha$-(trimethylsilyl)-styrene; the latter does not polymerize even under high pressure, in contrast to $\alpha$-methylstyrene which forms vitreous polymers under pressure.

The steric hindrances resulting from the presence of the naphthyl radical result in the fact that $\alpha$-$C_{10}H_7Si(CH_2CH=CH_2)_3$ and $\alpha$-$C_{10}H_7Si(OCH_2CH=CH_2)_3$ (Table 2) do not polymerize completely into solid vitreous products — trimers, chracteristic for polyalkenylsilanes with aliphatic radicals at the silicon atom — but form jelly-like polymers with a 15 and 31 % content of solid trimer.

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* Synthesized by P. S. Sanin.

From our investigations on disilanes (Table 3) capable of polymerization it was found that only 1,2-bis-(trimethoxysilyl)-ethylene formed a hexamer; an analogous monomer with methyl groups instead of methoxyl, does not polymerize [3]. In agreement with the general laws found for substituted ethylenes, 1-methyl-2-bis-(trimethylsilyl)-ethylene (a 1,2-substituted ethylene) cannot polymerize whereas 1,1-bis-(trimethylsilyl)-ethylene (a 1,1-substituted ethylene) which we previously [3] investigated formed a pentamer. 1,4-bis-(trimethylsilyl)-2-butene which has a symmetrical structure, also does not polymerize.

TABLE 3

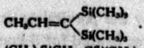
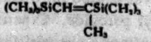
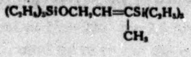
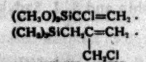
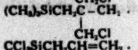
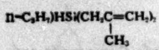
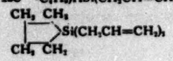
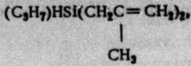
| Formula of the silicoolefin | Pressure (in atm.) | Concentration of initiator (mole %) | Polymerization products | | | |
|---|---|---|---|---|---|---|
| | | | External appearance of polymer obtained | Yield (as %) | Molecular wt. (mean) | Polymerization coefficient |
| $(CH_3O)_3SiCH{=}CHSi(OCH_3)_3$ . . . . . . | 6000 | 1 | dark oil - | 17 | 787 | 6 |
|  $CH_3CH{=}C\genfrac{}{}{0pt}{}{Si(CH_3)_3}{Si(CH_3)_3}$ . . . . . . . . . | 6000 | 1 | Not polymerized | | | |
|  $(CH_3)_3SiCH{=}\underset{\substack{\mid\\ CH_3}}{C}Si(CH_3)_3$ . . . . . . . . | 6000 | 1 | Not polymerized | | | |
| $(CH_3)_3SiCH_2CH{=}CHCH_2Si(CH_3)_3$ . . . | 6000 | 1 | Not polymerized | | | |
|  $(C_2H_5)_3SiOCH_2CH{=}\underset{\substack{\mid\\ CH_3}}{C}Si(C_2H_5)_3$ . . . . | 6000 | 1 | Not polymerized | | | |

TABLE 4

| Formula of silicoolefin | Pressure (in atm.) | Concentration of initiator (mole %) | Polymerization products | | | |
|---|---|---|---|---|---|---|
| | | | External appearance of polymer obtained | Yield (as %) | Molecular wt. (mean) | Polymerization coefficient |
| $(CH_3O)_3SiCH{=}CHCl$ . . . . . . . | 6000 | 3 | Dark mass | 45 | 490 | 3 |
| $(CH_3O)_3SiCCl{=}CH_2$ . . . . . . . . | 6000 | 3 | Dark viscous mass | 67 | Dissolves partially in benzene | |
| $(CH_3O)_3SiCCl{=}CH_2$ . . . . . . . . | 1 | 3 | The same | 37 | 676 | 3 |
|  $(CH_3)_3SiCH_2\underset{\substack{\mid\\ CH_2Cl}}{C}{=}CH_2$ . . . . . . . . | 6000 | 3 | Dark mass | 14 | 475 | 3 |
|  $(CH_3)_3SiCH_2\underset{\substack{\mid\\ CH_2Cl}}{C}-CH_3$ . . . . . . . . | 1 | 3 | The same | 2.8 | 368 | 2 |
| $CCl_3SiCH_2CH{=}CH_2$ . . . . . . . . | 6000 | 1 | Not polymerized | | | |
| $CCl_2Si(CH_2CH{=}CH_2)_2$ . . . . . . . | 6000 | 1 | Colorless resin | 29 | Trimer | |
|  $n\text{-}C_3H_7)HSi(CH_2\underset{\substack{\mid\\ CH_3}}{C}{=}CH_2)_2$ . . . . . | 6000 | 3 | Viscous, transparent, colorless resin | 85.5<br>14.5 | 1388<br>Trimer | 8 |
| $iso\text{-}C_3H_7)HSi(CH_2CH{=}CH_2)_2$ . . . | 6000 | 3 | Transparent, colorless glass | ~100 | Trimer | |
| $n\text{-}\text{-}C_4H_9)HSi(CH_2CH{=}CH_2)_2$ . . . . | 6000 | 3 | The same | ~100 | Trimer | |
| $iso\text{-}\ \text{-}C_4H_9)HSi(CH_2CH{=}CH_2)_2$ . . . | 6000 | 3 | The same | ~100 | Trimer | |
|  . . . . | 6000 | 3 | The same | ~100 | Trimer | |

In addition to silicohydrocarbon compounds we also studied silicoolefins containing halogen (Table 4). Of these compounds, 1-trimethoxysilyl-2-chloroethylene formed a trimer; meanwhile, it had been previously [3] established that 1-trialkylsilyl-2-chloroethylene cannot polymerize. This fact, like that mentioned above in the case of disilanes, indicates the positive influence of alkoxyl groups on the polymerization capacity. At the same time a comparison of the polymerization results of chloroalkenylsilanes (trichloroallylsilane and dichlorodiallylsilane) (Table 3) on the one hand, and the corresponding alkylalkenylsilanes [3] on the other hand, indicates that the chlorine atoms connected with the silicon atom exert a negative influence on the polymerization capacity.

The investigation of the dialkenylsilanes, such as  $(C_3H_7)HSi(CH_2\underset{CH_3}{\underset{|}{C}}=CH_2)_2$, $(n\text{-}C_4H_9)HSi(CH_2CH=CH_2)_2$ and others (Table 4) confirmed the facts [3, 4] which we had repeatedly noted, namely that alkenylsilanes with methallyl radicals at the silicon atom have a lesser tendency to polymerize than the corresponding alkenylsilanes containing allyl radicals in the same position.

Propyldimethallylsilane forms an 85 % soluble polymer (octamer) in contrast with other diallylsilanes which polymerize completely into trimers.

## EXPERIMENTAL

The investigation of the polymerization of silicoolefins was carried out by the previously described method [1, 3] with slight alterations in the conditions. The freshly-distilled monomer was heated for 6 hours at 120° under pressure of 6000 atm. in the presence of a polymerization initiator, tertiary butyl peroxide. Experiments without the use of pressure were carried out for comparative purposes. The polymers obtained were purified by removing the unreacted monomer under vacuum. The molecular weight was determined by the cryoscopic method in benzene.

## SUMMARY

1. The influence of various radicals at the silicon atom on the degree of polymerization of trialkylvinylsilanes was shown. It was established that compounds containing ethyl and methoxyl groups at the silicon atom have a greater tendency to polymerize than analogous compounds with other radicals (methyl. propyl, etc.).

2. The laws concerning the influence of substituents on the tendency of substituted ethylenes to polymerize, which were established for hydrocarbon monomers, were confirmed by the examples of silicoolefins.

## LITERATURE CITED

[1] A. D. Petrov, A. M. Polyakova, A. A. Sakharova, V. V. Korshak, V. F. Mironov and G. I. Nikishin, Proc. Acad. Sci. USSR 99, No. 5, 785 (1954).

[2] V. V. Korshak, A. D. Petrov, N. G. Matveeva, V. F. Mironov, G. I. Nikishin and S. I. Sadykh-Zade, J. Gen. Chem. 26, 1209 (1956).*

[3] A. M. Polyakova, V. V. Korshak, A. A. Sakharova, A. D. Petrov, V. F. Mironov, and G. I. Nikishin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 979.*

[4] V. V. Korshak, A. M. Polyakova, A. D. Petrov and V. F. Mironov, Proc. Acad. Sci. USSR, 112, 436 (1957).*

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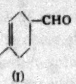
* Originar Russian pagination. See C.B. Translation.

# CONDENSATION OF $\Delta^3$-TETRAHYDROBENZALDEHYDES WITH ACETONE AND TRANSFORMATION OF THE PRODUCTS OF THIS CONDENSATION

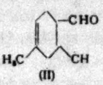
I. N. Nazarov,* G. P. Kugatova, and G. A. Laumenskas

A large number of studies [1-3] have been devoted to the condensation of aldehydes with acetone under the influence of alkaline agents. Of especial interest is the condensation of various substituted tetrahydrobenzaldehydes with acetone, since the products of this condensation – analogs and homologs of β-ionone [4, 5] – can be used as intermediates in the synthesis of analogs and homologs of vitamin A. The most convenient method of obtaining $\Delta^3$-tetrahydrobenzaldehydes are diene condensations, which were utilized by us in the present study.

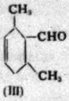
The heating of an equimolar mixture of isoprene and trans-piperylene with acrolein or crotonaldehyde in a metal ampul at 170-220° for 2.5 hrs gave the corresponding $\Delta^3$-tetrahydrobenzaldehydes (I), (II) and (III) in 60-80% yield, used by us to run the contemplated investigations.



(I)

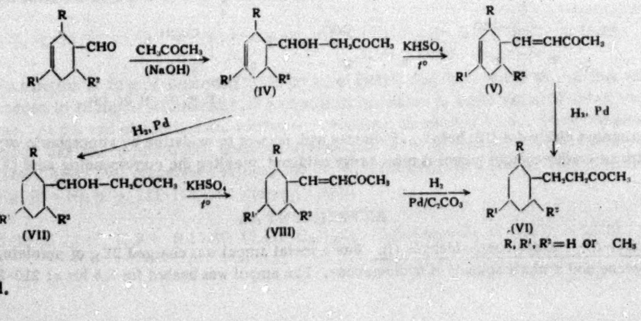


(II)



(III)

In the presence of dilute sodium hydroxide solution at a temperature of −2 to −5° these aldehydes enter into the aldol condensation with acetone and give the corresponding keto alcohols (IV) in 60-70% yield, the dehydration of which with potassium bisulfate gave the unsaturated ketones (V) in high yield. In contrast to the starting aldehydes (I-III) the unsaturated ketones (V) are easily hydrogenated with Pd catalyst, absorbing 2 moles of hydrogen with transformation into the saturated ketones (VI). The keto alcohols (IV) are also easily hydrogenated in the presence of palladium catalyst to yield the saturated keto alcohols (VII), the dehydration of which yields the unsaturated ketones (VIII) in about 80% yield, and the latter on hydrogenation yield the above mentioned saturated ketones (VI).



R
-CHO
R$^1$
R$^2$
CH$_3$COCH$_3$
(NaOH)
R
-CHOH–CH$_2$COCH$_3$
R$^1$
R$^2$
(IV)
KHSO$_4$
t°
R
-CH=CHCOCH$_3$
R$^1$
R$^2$
(V)
H$_2$, Pd
H$_2$, Pd
R
-CHOH–CH$_2$COCH$_3$
R$^1$
R$^2$
(VII)
KHSO$_4$
t°
R
-CH=CHCOCH$_3$
R$^1$
R$^2$
(VIII)
H$_2$
Pd/C$_2$CO$_3$
R
-CH$_2$CH$_2$COCH$_3$
R$^1$
R$^2$
(VI)
R, R$^1$, R$^2$=H or CH$_3$

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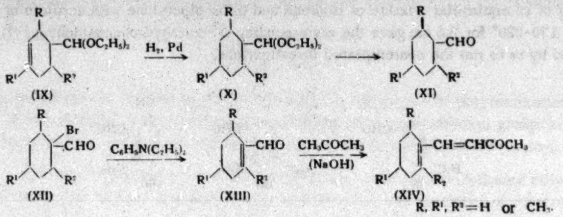
* Deceased.

The ease of dehydration of keto alcohols (IV) and (VII) depends on the position of the methyl groups in the cyclohexane ring and the keto alcohols with two ortho-methyl groups, obtained from aldehyde (III), are dehydrated with considerably more difficulty. It is also necessary to mention that the condensation of aldehydes (II) and (III), obtained at a temperature above 200°, with acetone leads to the formation of a difficultly separable mixture of keto alcohols (IV) and unsaturated ketones (V), which is explained by the presence of the cis-isomers as impurities in these aldehydes, obtained at elevated temperatures.

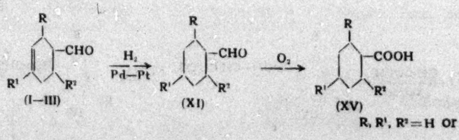
To shift the double bond in aldehydes (I-III) into conjugation with the aldehyde group we utilized the method described in the literature [6], consisting in the hydrogenation, bromination and dehydrobromination of the starting aldehydes (I-III). However, in contrast to the above described compounds (IV), (V) and (VIII), aldehydes (I-III) are hydrogenated with great difficulty in the presence of Pd catalyst, and here only 60-70% of the required hydrogen is absorbed. Even when the hydrogenation is run in an autoclave at a pressure of 100 atmos and a temperature of 60-80° in the presence of Pd catalyst the aldehydes (I-III) also absorb only 60-70% of the theoretical amount of hydrogen. Similar observations relative to some other examples have been mentioned in the literature [7]. Consequently, the unsaturated aldehydes (I-III) were first converted in the usual manner [8] into the corresponding acetals (IX), which already show smooth hydrogenation with Pd catalyst, absorbing 1 mole of hydrogen to form the saturated acetals (X). The latter when hydrolyzed readily give the pure saturated aldehydes (XI), which when brominated in chloroform are converted into the bromoaldehydes (XII), giving when heated with diethylaniline the unsaturated aldehydes (XIII) with conjugated bonds. The condensation of these aldehydes with acetone gave the corresponding analogs of β-ionone (XIV).



R, R', R² = H or CH$_3$.

When hydrogenated in the presence of Pd catalyst the unsaturated ketones (XIV) smoothly absorb 2 moles of hydrogen to yield the saturated ketones (VI) described above.

In making a detailed study of the conditions for the hydrogenation of aldehydes (I-III) in the presence of various catalysts we found that these aldehydes are smoothly hydrogenated if two different catalysts are added in sequence – first palladium on calcium carbonate, and then Adams platinum oxide [9], and with such conditions the pure saturated aldehydes (XI) are formed in nearly quantitative yield, being oxidized by atmospheric oxygen to the corresponding acids (XV).



R, R', R² = H or CH$_3$.

The saturated aldehydes (XI) behave differently with respect to oxidation by atmospheric oxygen and the aldehyde with two ortho-methyl groups is most easily oxidized, yielding the corresponding acid (XV) with m. p. 74-75°.

## EXPERIMENTAL

4-Methyl-Δ³-tetrahydrobenzaldehyde (I). Into a metal ampul was charged 21 g of acrolein, 33 g of freshly distilled isoprene and a small amount of hydroquinone. The ampul was heated for 2.5 hrs at 210-220°. Vacuum-distillation of the condensation product gave 42 g of (I) with b. p. 73-75° at 20 mm, $n_D^{16}$ 1.4743. The semicarbazone of the obtained aldehyde melts at 141-141.5° (from methanol); the 2,4-dinitrophenylhydrazone melts at 163.5-164.5° (from ethanol).

2,4-Dimethyl-$\Delta^3$-tetrahydrobenzaldehyde (II). Into a metal ampul was charged 30 g of crotonaldehyde, 30 g of isoprene and a small amount of hydroquinone. The ampul was heated for 2.5 hrs at 170-180°. Vacuum-distillation of the condensation product gave 48 g of (II) with b. p. 66-68° at 10 mm; $n_D^{25.5}$ 1.4716.

Found %: C 78.04, 78.17; H 10.13, 10.37. $C_9H_{14}O$. Calculated %: C 78.26; H 10.14.

The semicarbazone of the obtained aldehyde melts at 172-173° (from methanol).

Found %: N 21.65, 21.76. $C_{10}H_{17}ON_3$. Calculated %: N 21.43.

The 2,4-dinitrophenylhydrazone melts at 159-160°.

2,6-Dimethyl-$\Delta^3$-tetrahydrobenzaldehyde (III). A mixture of 25 g of trans-crotonaldehyde, 30 g of trans-piperylene (obtained by the isomerization of technical piperylene with iodine, b. p. 42°, $n_D^{19}$ 1.4298) and a small amount of hydroquinone was heated in a metal ampul at 190-200° for 2.5 hrs. Distillation of the condensation products gave 32 g of (III) with b. p. 75.5-77° at 14 mm, $n_D^{16}$ 1.4690.

Found %: C 77.96, 78.00; H 10.14, 10.03. $C_9H_{14}O$. Calculated %: C 78.26; H 10.14.

The 2,4-dinitrophenylhydrazone of the obtained aldehyde melts at 166-167.5°.

Condensation of $\Delta^3$-tetrahydrobenzaldehydes (I-III) with acetone. a) To a solution of 10 g of aldehyde (I) in 20 ml of freshly distilled acetone at −3° and with vigorous stirring was added in 15 min a solution of 0.97 g of sodium hydroxide in a mixture of 31 ml of water and 77 ml of acetone. After this the temperature of the reaction mixture was raised to room temperature in 45 min, and the stirring was continued for another 2 hrs. The reaction mixture was poured into water, acidified with sulfuric acid, the product extracted with ether, washed twice with water, dried over magnesium sulfate, and vacuum-distilled. We obtained 8.8 g of keto alcohol (IV) ($R^1 = CH_3$; $R = R^2 = H$) with b. p. 105-108° at 1 mm, $n_D^{19}$ 1.4945.

Found %: C 72.57, 72.59; H 9.75, 9.89. $C_{11}H_{18}O_2$. Calculated %: C 72.53; H 9.89.

The semicarbazone of the obtained keto alcohol melts at 126-127° (from methanol).

b) To a solution of 14.5 g of aldehyde (II) in 30 ml of freshly distilled acetone at −3° and with vigorous stirring was added in 20 min a solution of 1.4 g of sodium hydroxide in a mixture of 115 ml of acetone and 46 ml of water. After this the temperature of the reaction mixture was raised to room temperature in 50 min, and the stirring was continued for another 2 hrs. The reaction mixture was poured into water, acidified with sulfuric acid, the product extracted with ether, washed three times with water, dried over magnesium sulfate, and vacuum-distilled. We obtained 13.8 g of keto alcohol (IV) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 122-125° at 1.5 mm, $n_D^{18}$ 1.4935.

Found %: C 73.74, 73.63; H 10.25, 10.36. $C_{12}H_{20}O_2$. Calculated %: C 73.47; H 10.20.

c) To a solution of 20 g of aldehyde (III) in 45 ml of freshly distilled acetone at −4° and with vigorous stirring was added in 18 min a solution of 1.95 g of sodium hydroxide in a mixture of 65 ml of water and 155 ml of acetone. At the end of addition the stirring was continued for another 4 hrs at room temperature. The reaction mixture was poured into water, acidified with sulfuric acid, the product extracted with ether, washed twice with water, dried over magnesium sulfate, and vacuum-distilled. We obtained 19 g of keto alcohol (IV) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 111-113° at 1 mm, $n_D^{17}$ 1.4910.

Found %: C 73.48, 73.53; H 10.39, 10.41. $C_{12}H_{20}O_2$. Calculated %: C 73.47; H 10.20.

Hydrogenation of keto alcohols (IV). a) A solution of 25 g of keto alcohol (IV) ($R^1 = CH_3$; $R = R^2 = H$) in 50 ml of methyl acetate was hydrogenated in the presence of $Pd/CaCO_3$ catalyst. In three hrs 3.09 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 22.1 g of saturated keto alcohol (VII) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 93-95° at 1 mm, $n_D^{17}$ 1.4720.

Found %: C 71.96, 71.83; H 10.94, 10.94. $C_{11}H_{20}O_2$. Calculated %: C 71.74; H 10.87.

b) A solution of 5 g of keto alcohol (IV) ($R^1 = R^2 = CH_3$; $R = H$) in 10 ml of methanol was hydrogenated in the presence of $Pd/CaCO_3$, catalyst. The amount of hydrogen absorbed was 0.62 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 4.6 g of saturated keto alcohol (VII) ($R^1 = R^2 = CH_3$; $R = H$) b. p. 112-114° at 1 mm, $n_D^{18}$ 1.4740.

c) A solution of 5 g of keto alcohol (IV) ($R = R^2 = CH_3$; $R^1 = H$) in methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed was 0.57 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 4.7 g of saturated keto alcohol (VII)($R = R^2 = CH_3$; $R^1 = H$), b. p. 106-107° at 1 mm, $n_D^{16}$ 1.4790.

Found %: C 72.51, 72.47; H 11.24, 11.26. $C_{12}H_{22}O_2$. Calculation %: C 72.72; H 11.11.

Dehydration of keto alcohols (IV). a) A mixture of 5 g of keto alcohol (IV) ($R' = CH_3$; $R = R^2 = H$) and 1.2 g of fused powdered potassium bisulfate was heated in a vacuum of 70 mm at 135-140° for 30 min. Toward the end of heating the vacuum was increased, and the dehydration product was distilled. We obtained 3.4 g of unsaturated ketone (V) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 84° at 1 mm, $n_D^{17}$ 1.5040.

Found %: C 80.31, 80.40; H 9.99, 9.90. $C_{11}H_{16}O$. Calculated %: C 80.48; H 9.75.

b) A mixture of 5 g of keto alcohol (IV) ($R^1 = R^2 = CH_3$; $R = H$) and 0.8 g of fused powdered potassium bisulfate was heated in a vacuum of 70 mm at 130-140° for 30 min. Toward the end of heating the vacuum was increased. After two distillations we obtained 3.7 g of unsaturated ketone (V) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 95-96° at 1 mm, $n_D^{19}$ 1.4980.

Found %: C 80.82, 80.59; H 10.24, 10.18. $C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11.

c) A mixture of 4 g of keto alcohol (IV) ($R = R^2 = CH_3$; $R^1 = H$) and 0.7 g of fused powdered potassium bisulfate was heated in a vacuum of 70-80 mm for 30 min at 130-140°, after which the product was distilled (b. p. 101-105° at 1 mm; $n_D^{17}$ 1.4890). To the distilled product was added 0.4 g of potassium bisulfate, and the mixture was again heated in a vacuum of 70 mm at 130-140° for 15 min. After two distillations we isolated 2.9 g of the unsaturated ketone (V) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 91-92.5° at 1 mm, $n_D^{17}$ 1.4969.

Found %: C 80.63, 80.91; H 10.14; 10.33. $C_{12}H_{18}O$. Calculated %: C 80.9; H 10.11.

Dehydration of keto alcohols (VII). a) A mixture of 3 g of keto alcohol (VII) ($R^1 = CH_3$; $R = R^2 = H$) and 0.8 g of fused powdered potassium bisulfate was heated in a vacuum of 70 mm at 135-140° for 30 min. On distillation we obtained 2.5 g of the unsaturated ketone (VIII) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 105-108° at 7 mm; $n_D^{20}$ 1.4774.

Found %: C 79.26, 79.27; H 10.98, 10.95. $C_{11}H_{18}O$. Calculated %: C 79.52; H 10.84.

b) A mixture of 4 g of keto alcohol (VII) ($R^1 = R^2 = CH_3$; $R = H$) and 0.7 g of fused powdered potassium bisulfate was heated in a vacuum of 85 mm at 134-140° for 30 min. On distillation we obtained 2.8 g of the unsaturated ketone (VIII) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 82° at 1 mm, $n_D^{15.5}$ 1.4825.

Found %: C 80.07, 80.07; H 11.15, 11.20. $C_{12}H_{20}O$. Calculated %: C 80.00; H 11.11.

c) A mixture of 4 g of keto alcohol (VIII) ($R = R^2 = CH_3$; $R^1 = H$) and 1 g of fused powdered potassium bisulfate was heated in a vacuum of 60 mm at 130-138° for 25 min. At the end of heating the vacuum was increased to 13 mm, and the product was distilled (b. p. 124° at 13 mm, $n_D^{18}$ 1.4851), after which 0.7 g of potassium bisulfate was added, and the mixture was heated in a vacuum of 70 mm at 130-140° for 15 min. After two distillations we obtained 2.9 g of the unsaturated ketone (VIII) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 121° at 12 mm, $n_D^{16}$ 1.4869, possessing a pleasant floral odor.

Found %: C 79.89, 80.19; H 11.16, 11.27. $C_{12}H_{20}O$. Calculated %: C 80.00;H 11.11.

Hydrogenation of unsaturated ketones (V). a) A solution of 1 g of ketone (V) ($R^1 = CH_3$; $R = R^2 = H$) in 3 ml of methanol was hydrogenated in the presence of $Pd/CaCO_3$ catalyst. The amount of hydrogen absorbed in 30 min was 0.28 liter, which corresponds to the hydrogenation of two double bonds. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 0.6 g of the saturated ketone (VI) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 77° at 1 mm, $n_D^{18}$ 1.4565.

Found %: C 78.58, 78.59; H 11.96, 12.03. $C_{11}H_{20}O$. Calculated %: C 78.57; H 11.9.

The semicarbazone of this ketone (VI) melts at 171-172° (from methanol).

Found %: N 18.63, 18.89. $C_{12}H_{23}ON_3$. Calculated %: N 18.66.

b) A solution of 2.3 g of ketone (V) ($R^1 = R^2 = CH_3$; $R = H$) in 7 ml of methanol was hydrogenated in the presence of $Pd/CaCO_3$ catalyst. The amount of hydrogen absorbed in 55 min was 0.59 liter, which corresponds to the hydrogenation of two double bonds. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 2 g of the saturated ketone (VI) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 103° at 5 mm, $n_D^{17}$ 1.4602.

Found %: C 79.13, 79.08; H 12.13, 12.10. $C_{12}H_{22}O$. Calculated %: C 79.13; H 12.09.

The semicarbazone of this ketone melts at 160.5-161° (from methanol).

c) A solution of 3.7 g of ketone (V) ($R = R^2 = CH_3$; $R^1 = H$) in 30 ml of methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed in 1.5 hrs was 0.96 liter, which corresponds to the hydrogenation of two double bonds. The solvent was distilled off, and the product was vacuum-distilled. We obtained 3.4 g of the saturated ketone (VI) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 96-96.5° at 1.5 mm, $n_D^{19}$ 1.4622.

Found %: C 79.00, 78.89; H 11.90, 11.98. $C_{12}H_{22}O$. Calculated %: C 79.12; H 12.09.

Hydrogenation of unsaturated ketones (VIII). a) A solution of 2.2 g of the unsaturated ketone (VIII) ($R^1 = CH_3$; $R = R^2 = H$) in 6 ml of methanol was hydrogenated in the presence of $Pd/CaCO_3$ catalyst. The amount of hydrogen absorbed was 0.29 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 1.6 g of the saturated ketone (VI) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 76-78° at 1 mm, $n_D^{20}$ 1.4560.

b) A solution of 1.2 g of the unsaturated ketone (VIII) ($R^1 = R^2 = CH_3$; $R = H$) in 4 ml of methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed in 45 min was 0.13 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 0.9 g of ketone (VI) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 84° at 1 mm, $n_D^{15}$ 1.4600. The semicarbazone of this ketone melts at 160.5-161° (from methanol).

c) A solution of 0.5 g of the unsaturated ketone (VIII) ($R = R^2 = CH_3$; $R^1 = H$) in 10 ml of methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed in 20 min was 70 ml, which corresponds to the hydrogenation of one double bond. The solvent was distilled off, and the product was vacuum-distilled. We obtained 0.3 g of the saturated ketone (VI) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 91° at 1 mm, $n_D^{19}$ 1.4620.

Preparation of acetals (IX). a) To a solution of 20 g of aldehyde (I) in 80 ml of anhydrous alcohol was added 0.5 ml of hydrochloric acid (d 1.21). The reaction mixture was allowed to stand for 2 days at room temperature, after which it was poured into water, containing 2 g of sodium carbonate. The obtained oil was separated, and the water layer was extracted with ether. The ethereal solution was combined with the oil, dried over magnesium sulfate, and vacuum-distilled. We obtained 12.5 g of the diethyl acetal (IX) ($R = R^2 = H$; $R^1 = CH_3$), b. p. 105-107° at 12 mm, $n_D^{14}$ 1.4565.

Found %: C 72.42, 72.33; H 11.46, 11.30. $C_{12}H_{22}O_2$. Calculated %: C 72.72; H 11.11.

b) To a solution of 20 g of aldehyde (II) in 80 ml of anhydrous alcohol was added 0.5 ml of hydrochloric acid (d 1.21). The reaction mixture was allowed to stand for 2 days at room temperature. After the usual treatment and vacuum-distillation we obtained 15.2 g of the diethyl acetal (IX) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 107-109°, at 11 mm, $n_D^{18}$ 1.4570.

Found %: C 73.73, 73.47; H 11.42, 11.42. $C_{13}H_{24}O_2$. Calculated %: C 73.58; H 11.32.

c) A solution of 30 g of aldehyde (III) in 120 ml of anhydrous ethyl alcohol was treated with 0.75 ml of hydrochloric acid (d 1.21). The reaction mixture was allowed to stand for 3 days at room temperature. After the usual treatment and vacuum-distillation we obtained 23 g of the diethyl acetal (IX) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 105° at 8 mm, $n_D^{19}$ 1.4540.

Found %: C 73.38, 73.42; H 11.42, 11.33. $C_{13}H_{24}O_2$. Calculated %: C 73.58; H 11.31.

Hydrogenation of acetals (IX). a) A solution of 13 g of diethyl acetal (IX) ($R = R^2 = H$; $R^1 = CH_3$) in 30 ml of methanol was hydrogenated in the presence of Pd/$CaCO_3$ catalyst. The amount of hydrogen absorbed in 3 hrs was 1.3 liters, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 12.5 g of the saturated diethyl acetal (X) ($R = R^2 = H$; $R^1 = CH_3$), b. p. 94-96° at 9 mm, $n_D^{15.5}$ 1.4445.

Found %: C 71.99, 71.89; H 12.11, 12.01. $C_{12}H_{24}O_2$. Calculated %: C 72.00; H 12.00.

b) A solution of 7.8 g of diethyl acetal (IX) ($R^1 = R^2 = CH_3$; $R = H$) in 16 ml of methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed in 2 hrs was 0.76 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 7.3 g of the saturated diethyl acetal (X) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 101-103° at 10 mm, $n_D^{19}$ 1.4458.

Found %: C 72.75, 73.07; H 11.98, 12.02. $C_{13}H_{26}O_2$. Calculated %: C 72.9; H 12.15.

c) A solution of 5.5 g of diethyl acetal (IX) ($R = R^2 = CH_3$; $R^1 = H$) in 15 ml of methanol was hydrogenated in the presence of palladium catalyst. The amount of hydrogen absorbed in 1 hr and 20 min was 0.63 liter, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 5.3 g of (X) ($R = R^2 = CH_3$; $R^1 = H$), b. p. 101-102° at 9 mm; $n_D^{17.5}$ 1.4469.

Found %: C 72.77, 72.59; H 12.17, 12.15. $C_{13}H_{26}O_2$. Calculated %: C 72.89; H 12.14.

Hydrolysis of acetals (X). a) A mixture of 6.8 g of diethyl acetal (X) ($R = R^2 = H$; $R^1 = CH_3$), 9 ml of acetic acid and 20 ml of 15% sulfuric acid was boiled under reflux for 5 hrs, after which the mixture was extracted with ether. The ether extract was washed with sodium carbonate solution, then with water, and finally dried over magnesium sulfate. The product was vacuum-distilled. We obtained 2.8 g of aldehyde (XI) ($R = R^2 = H$; $R^1 = CH_3$), b. p. 58° at 9 mm, $n_D^{20}$ 1.4492.

Found %: C 75.99, 75.98; H 11.25, 11.18. $C_8H_{14}O$. Calculated %: C 76.19; H 11.11.

The 2,4-dinitrophenylhydrazone of the obtained aldehyde melts at 183-184° (from ethanol).

Found %: N 18.53, 18.42. $C_{14}H_{18}O_4N_4$. Calculated %: N 18.30.

b) A mixture of 6 g of diethyl acetal (X) ($R^1 = R^2 = CH_3$; R =H), 8 ml of acetic acid and 16 ml of 23% sulfuric acid was boiled under reflux for 5 hrs, after which the mixture was extracted with ether. The ether extract was washed with sodium carbonate solution, then with water, and finally dried over magnesium sulfate. The product was vacuum-distilled. We obtained 2.8 g of aldehyde (XI) ($R^1 = R^2 = CH_3$; R = H), b. p. 70° at 8 mm, $n_D^{19}$ 1.4530.

c) A mixture of 5 g of diethyl acetal (X) ($R = R^2 = CH_3$; $R^1$ = H), 4 ml of acetic acid and 50 ml of 25% sulfuric acid was boiled under reflux. The product was extracted with ether, washed with 10% sodium carbonate solution, then with water, dried over magnesium sulfate, and finally vacuum-distilled. We obtained 2 g of aldehyde (XI) ($R = R^2 = CH_3$; $R^1$ = H), b. p. 80-81° at 14 mm, $n_D^{20}$ 1.4510. The 2,4-dinitrophenylhydrazone of this aldehyde melts at 130-130.5°.

Hydrogenation of aldehydes (I-III). a) A solution of 35 g of aldehyde (I) in 100 ml of methanol was hydrogenated in the presence of $Pd/CaCO_3$ catalyst. The hydrogenation was stopped when 2.5 liters of hydrogen had been absorbed, and some platinum catalyst ($PtO_2$) was added. In 16 hrs 6.35 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 34.5 g of aldehyde (XI) ($R = R^2$ = H; $R^1 = CH_3$), b. p. 58° at 9 mm, $n_D^{15}$ 1.4512. The 2,4-dinitrophenylhydrazone of the aldehyde melts at 183-184°.

b) A solution of 90 g of aldehyde (II) in methanol was hydrogenated in an autoclave at 60° and a pressure of 100 atmos in the presence of $Pd/CaCO_3$ catalyst. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 67 g of a fraction with b. p. 89-95° at 18 mm, $n_D^{25}$ 1.4595. A solution of 20 g of this fraction in 50 ml of methanol was hydrogenated in the presence of platinum catalyst. The amount of hydrogen absorbed was 2.5 liters. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was vacuum-distilled. We obtained 18.2 g of aldehyde (XI) ($R^1 = R^2 = CH_3$; R = H), b. p. 96-98° at 17 mm, $n_D^{19}$ 1.4528.

c) A solution of 6.8 g of aldehyde (III) in 20 ml of methanol was hydrogenated in the presence of palladium catalyst. After 0.56 liter of hydrogen had been absorbed the hydrogenation was stopped and some platinum catalyst was added. In 10 hrs a total of 1.16 liters of hydrogen was absorbed, which corresponds to the hydrogenation of one double bond. The catalyst was filtered, the solvent was distilled off, and the hydrogenation product was distilled. We obtained 6.4 g of aldehyde (XI) ($R = R^2 = CH_3$; $R^1$ = H), b. p. 66-67° at 8 mm, $n_D^{20}$ 1.4510. The 2,4-dinitrophenylhydrazone of the aldehyde melts at 130-130.5°.

Preparation of unsaturated aldehydes (XIII). a) To a mixture of 30 g of aldehyde (XI) ($R = R^2$ = H; $R^1 = CH_3$), 80 ml of chloroform and 18 g of calcium carbonate was added at 9-15° and with vigorous stirring a solution of 40 g of bromine in 60 ml of chloroform. After all of the bromine solution had been added the stirring was continued for another 3 hours at room temperature. The chloroform layer was separated, and the remainder was extracted with chloroform. The combined chloroform extract was washed with sodium bicarbonate solution, then with sodium thiosulfate solution, next with water, and finally it was dried over magnesium sulfate. The bromination product was vacuum-distilled. We obtained 24.6 g of bromoaldehyde (XII) ($R = R^2$ = H; $R^1 = CH_3$) b. p. 58-59° at 2 mm, $n_D^{18}$ 1.4930. A mixture of 16 g of this bromoaldehyde with 35 g of diethylaniline was boiled for 2 minutes in a stream of nitrogen and then cooled rapidly in a mixture of ice and salt. The crystallized diethylaniline hydrobromide was dissolved in water. The excess base was removed by treatment with dilute sulfuric acid. The product was extracted with ether, washed with sodium bicarbonate solution, dried over magnesium sulfate, and vacuum-distilled. We obtained 2.7 g of aldehyde (XIII) ($R = R^2$ = H; $R^1 = CH_3$) b. p. 75° at 14 mm, $n_D^{16}$ 1.4842.

Found %: C 77.05; H 10.03. $C_8H_{12}O$. Calculated %: C 77.42; H 9.68.

The 2,4-dinitrophenylhydrazone of the obtained aldehyde melts at 196.5-198°.

Found %: N 18.14, 18.28. $C_{14}H_{16}O_4N_4$. Calculated %: N 18.42.

b) To a mixture of 15 g of aldehyde (XI) ($R^1 = R^2 = CH_3$; R = H), 40 ml of chloroform and 9 g of calcium carbonate was added at 15-18° and with vigorous stirring a solution of 20 g of bromine in 30 ml of chloroform. After all of the bromine solution had been added the stirring was continued for another 3 hrs. After the bromination product had been treated in the usual manner and distilled we obtained 11 g of bromoaldehyde (XII) ($R^1 = R^2 = CH_3$; R = H), b. p. 79-83° at 1 mm, $n_D^{20}$ 1.4988. A mixture of 5.7 g of the obtained bromoaldehyde and 14 g of diethylaniline was boiled for 2 min in a stream of nitrogen and then cooled rapidly. The crystallized diethylaniline hydrobromide was dissolved in water. The excess base was removed by treatment with dilute sulfuric acid. The product was extracted with ether, washed with sodium bicarbonate solution, dried over magnesium sulfate, and vacuum-distilled. We obtained 1.9 g of aldehyde (XIII) ($R^1 = R^2 = CH_3$; R = H), b. p. 94-96° at 15 mm, $n_D^{20}$ 1.4961.

Found %: C 78.20, 78.00; H 10.16, 9.97. $C_9H_{14}O$. Calculated %: C 78.26; H 10.14.

c) To a mixture of 18 g of aldehyde (XI) ($R = R^2 = CH_3$; $R^1$ = H), 48 ml of chloroform and 10.8 g of calcium carbonate was added at 10-15° a solution of 24 g of bromine in 36 ml of chloroform. After all of the bromine had been added the mixture was stirred for another 4 hrs. After the usual treatment and distillation of the bromination product we obtained 23.8 g of bromoaldehyde (XII) ($R = R^2 = CH_3$; $R^1$ = H), b. p. 68-70° at 1 mm, $n_D^{18}$ 1.4952. A mixture of 23 g of the obtained bromoaldehyde and 54 g of diethylaniline was boiled for 2 min in a stream of nitrogen and then cooled rapidly. The crystallized diethylaniline hydrobromide was dissolved in water. The excess base was removed by treatment with dilute sulfuric acid. The product was extracted with ether, washed with sodium bicarbonate solution, dried over magnesium sulfate, and vacuum-distilled. We obtained 10.2 g of aldehyde (XIII) ($R = R^2 = CH_3$; $R^1$ = H), b. p. 86-99° at 9 mm, $n_D^{20}$ 1.4972-1.5096. After purification through the semicarbazone, aldehyde (XIII) ($R = R^2 = CH_3$; $R^1$ = H) had b. p. 94-95° at 17 mm, $n_D^{20}$ 1.5045.

Found %: C 78.38, 78.23; H 10.24, 10.12. $C_9H_{14}O$. Calculated %: C 78.26; H 10.14.

The semicarbazone of the obtained aldehyde melts at 209-210° (from ethanol).

Condensation of aldehydes (XIII) with acetone. a) Three grams of aldehyde (XIII) ($R = R^2$ = H; $R^1 = CH_3$) was dissolved in 6 ml of acetone and to the solutionat −3° and with vigorous stirring was added in 10 min a solution of 0.2 g of sodium hydroxide in a mixture of 9.3 ml of water and 23 ml of acetone. After this addition the stirring was continued at room temperature for another 3 hrs. The reaction mixture was poured into water, acidified with hydrochloric acid, the product extracted with ether, washed three times with water, dried over magnesium sulfate, and vacuum-distilled. We obtained 2.5 g of product with b. p. 86-90° at 1 mm, $n_D^{14}$ 1.5363. This fraction was redistilled from potassium bisulfate. We obtained 1.7 g of ketone (XIV) ($R = R^2$= H; $R^1 = CH_3$), b. p. 88° at 1 mm, $n_D^{13}$ 1.5390.

Found %: C 80.65, 80.60; H 9.95, 9.72. $C_{11}H_{16}O$. Calculated %: C 80.48; H 9.76.

b) To a solution of 1.8 g of aldehyde (XIII) ($R^1 = R^2 = CH_3$; R = H) in 4 ml of freshly distilled acetone was added at −3°, with vigorous stirring, in 7 min, a solution of 0.2 g of sodium hydroxide in a mixture of 15.4 ml of acetone and 6.2 ml of water. After this the temperature of the reaction mixture was raised to room temperature in 30 minutes and the stirring was continued for another 2 hrs. The reaction mixture was poured into water, acidified with sulfuric acid, the product extracted with ether, washed three times with water, dried over magnesium sulfate, and vacuum-distilled. Redistillation from potassium bisulfate gave 0.7 g of ketone (XIV) ($R^1 = R^2 = CH_3$; R = H), b. p. 91-92° at 1 mm, $n_D^{20}$ 1.5130.

Found %: C 80.69; H 10.08. $C_{12}H_{18}O$. Calculated %: C 80.89; H 10.1.

c) To a solution of 2 g of aldehyde (XIII) ($R = R^2 = CH_3$; $R^1$ = H) in 4 ml of acetone was added at −4°, with vigorous stirring, in 10 min, a solution of 0.2 g of sodium hydroxide in a mixture of 15.5 ml of acetone and 6.5 ml of water. After this the temperature of the reaction mixture was raised to room temperature in 30 min and the stirring was maintained for another 3 hrs. The reaction mixture was poured into water acidified with sulfuric acid, the product extracted with ether, washed with water, dried over magnesium sulfate, and vacuum-distilled. Redistillation from potassium bisulfate gave 0.9 g of unsaturated ketone (XIV) ($R = R^2 = CH_3$; $R^1$ = H), b. p. 92-93° at 1 mm, $n_D^{20}$ 1.5198.

Oxidation of aldehydes (XI). a) Aldehyde (XI) ($R^1 = CH_3$; $R = R^2 = H$) in an amount of 2.2 g was allowed to stand in the air. After 3 days the mass was mostly crystalline. After recrystallization from dilute acetic acid we obtained 2 g of acid (XV) ($R^1 = CH_3$; $R = R^2 = H$), b. p. 110.5-111.5°.

Found %: C 67.59, 67.35; H 10.00, 9.99. $C_8H_{14}O_2$. Calculated %: C 67.50; H 9.86.

b) Two grams of aldehyde (XI) ($R^1 = R^2 = CH_3$; $R = H$) was allowed to stand in the air. At the end of 6.5 days the mass was vacuum-distilled to yield 1.3 g of acid (XV) ($R^1 = R^2 = CH_3$; $R = H$), b. p. 107-108° at 2.5 mm, $n_D^{21}$ 1.4590.

Found %: C 69.04, 69.08; H 10.35, 10.48. $C_9H_{16}O_2$. Calculated %: C 69.23; H 10.32.

c) Five grams of aldehyde (XI) ($R = R^2 = CH_3$; $R^1 = H$) was allowed to stand in the air. After 5 days the mass was mostly crystalline. We obtained 4.3 g of acid (XV) ($R = R^2 = CH_3$; $R^1 = H$), which after recrystallization from dilute acetic acid had m. p. 74-75°.

Found %: C 68.89, 68.96; H 10.34, 10.34. $C_9H_{16}O_2$. Calculated %: C 69.23; H 10.32.

## SUMMARY

1. $\Delta^3$-Tetrahydrobenzaldehydes (I-III) in presence of dilute sodium hydroxide solution enter into aldol condensation with acetone, forming the keto alcohols (IV) in 60-70% yield. The dehydration of these keto alcohols gives the unsaturated ketones (V) in high yields.

2. Under the same conditions the $\Delta^1$-tetrahydrobenzaldehydes (XIII) with acetone show for the most part the crotonic type of condensation and form the unsaturated ketones (XIV) in 50-60% yield.

3. The hydrogenation of aldehydes (I-III), their acetals (IX), the keto alcohols (IV), and ketones (V) and (VIII), has been described.

## LITERATURE CITED

[1] G. Merling and R. Walde, Lieb. Ann. 366, 123 (1909).

[2] E. C. Horning, M. G. Horning and E. J. Platt, J Amer. Soc. 71, 1771 (1949).

[3] O. Diels and K. Alder, Lieb. Ann. 470 62 (1929).

[4] P. P. Shorygin and A. Gusev, J. Gen. Chem. 6, 1569 (1936).

[5] B. A. Arbuzov, Z. Zinovyeva, and I. Frank, J. Gen. Chem. 17, 2278 (1937).

[6] I. Heilbron, E. R. H. Jones, R. W. Richardson, and F. Sondheimer, J. Chem. Soc. 1949, 737.

[7] J. C. Lunt and F. Sondheimer, J. Chem. Soc. 1950, 2957.

[8] Houben, Methods of Organic Chemistry, III, Vol. 1.*

[9] Organic Syntheses, II, P. 192. *

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# MECHANISM OF THE CATALYTIC ACTION OF ALUMINUM CHLORIDE

## V. REACTIVITY OF AROMATIC COMPOUNDS IN ALKYLATION

N. N. Lebedev

The reactivity of aromatic compounds in their alkylation by the Friedel-Crafts method has been studied to a much lesser degree than have other reactions of substitution in the aromatic ring.

Olivier and Berger [1] determined the relative reaction rates of p-nitrobenzyl chloride with chlorobenzene, benzene and toluene (0.187 : 1 : 2.33); however, they ran their experiments in these compounds as the medium, and consequently the effect of the solvent should be considered in their results. From the composition of the reaction products of ethylene with benzene Francis and Reid [2] assumed that the alkylation rate of benzene was the same as that of its ethylated homologs. This method evokes great doubt due to the reversible nature of the reaction. Condon [3] determined the absorption rate of propylene in nitromethane solutions of some alkylbenzenes in the presence of aluminum chloride. He gives the following values for the reactivities (benzene 1.0): toluene 2.1, ethylbenzene 1.8, isopropylbenzene 1.7, tert-butylbenzene 1.4. However, the results obtained by Condon could have been affected by the influence of diffusion factors during solution of the propylene in the reaction mass. Brown and Grayson [4] recently found the relative reaction rates of 3,4-dichlorobenzyl chloride with chlorobenzene, benzene, toluene and m-xylene in nitrobenzene solution to be equal to 0.47, 1.00, 1.64, and 2.08, respectively.

The reactivity of other aromatic compounds has not been studied. In general, the literature contains very little quantitative data on the rate of the alkylation reaction and only 2-3 values for the activation energy. To fill in this gap and make a more extensive study of the problem are the purpose of this paper.

## METHOD OF OPERATION

The reactivities of different aromatic compounds were determined by the method of directly measuring their rates of reaction with cyclohexyl chloride in a nitrobenzene solution of aluminum chloride. The apparatus used for this purpose and the entire method of operation and calculations have already been described in one of our earlier papers [5]. In all of the experiments described in this paper the initial cyclohexyl chloride concentration was 0.200 mole/liter, and in order to avoid polyalkylation of the aromatic compound the chloride was taken in 6 to 8-fold excess, which made it an important component of the solvent. In view of the earlier shown [5] strong influence exerted by the medium on the alkylation rate a variation in the molar volumes of the aromatic compounds could be responsible for obtaining inaccurate results if the experiments were run with the same volume or molar concentrations of the aromatic compounds. For this reason we ran the experiments using a constant mole fraction of nitrobenzene and aromatic compound, on the assumption that in such a case there is greater assurance that constant properties for the reaction medium would be retained. In all of the experiments described in this paper the mole fraction of nitrobenzene was 0.839, which corresponds to a medium in which the benzene concentration is 12.4 vol. %, this being the concentration used in a previous study [5]. Here the molar concentrations of the compounds being alkylated differed among themselves, which made it necessary to compare the reactivities of the studied compounds on the basis of the rate constants for a second order reaction: $dx/dt = k_2[RCl][ArH]$, which were calculated by dividing the directly determined monomolecular rate constants by the concentration of the aromatic compound. In the tables below, where the experimental results are presented, the values of these rate constants are given with an indication of the number of parallel measurements made and the average error. Each separate experiment was run in such a manner that from 5 to 9 separate points were obtained to calculate the rate constant, while the maximum degree of reaction completion varied from 46 to 85%. The temperature was controlled with an accuracy of ± 0.05°. The total volume of the reaction mass was kept equal to 20.0 ml in all cases.

By means of special experiment it was shown that commercial (either pure or chemically pure grades) toluene, ethylbenzene, isopropylbenzene, chlorobenzene and bromobenzene do not require special chemical purification [6], since the reaction rates after such purification did not increase. However, both the p- and m-xylenes had to be purified by treatment with sulfuric acid. Fluorobenzene, iodobenzene and the o-, m- and p-chlorotoluenes were first treated with sulfuric acid, and then with 10% caustic solution. The last reagent was also used to wash the anisole. The sec- and tert-butylbenzenes and phenylcyclohexane were obtained by the Friedel-Crafts reaction and consequently did not require special purification. All of the enumerated compounds, including those not subjected to chemical purification, prior to use were either distilled through a fractionation column with an efficiency of 17 theoretical plates or they were distilled twice from a flask with dephlegmator, collecting not more than 50% of the product each time. The fractions were collected in a boiling point range not exceeding 0.5-1.0°. Diphenylmethane was purified by fractional crystallization, while the other solids – 1,2-diphenylethane, 1,4-diphenylbutane and naphthalene – were purified by recrystallization from ethyl alcohol.

The essential feature in the preparation of the starting compounds is their degree of drying. The latter was checked by the amount of hydrogen chloride evolved when a blank sample (in the absence of the halo derivative) was blown for 10 min. This amount should not exceed 0.5 to 1.0 ml of 0.1 N solution. The desired degree of drying was usually achieved in the distillation, and for the liquid hydrocarbons, sodium was used in addition.

It should be mentioned that such constants for the starting compounds as the refractive index, boiling point and melting point are not a sufficient criterion of their purity. The best criterion for this proved to be the coefficient of increase in the reaction rate when the aluminum chloride concentration was changed from 0.100 to 0.203 mole/liter. According to our data [5], in nitrobenzene medium it is equal to 1.35-1.40, in which connection its increase indicates the presence of impurities in the product, which exert a greater deactivating influence on the catalyst the smaller its concentration. In such cases it was necessary to purify the compound further by the above described method until a further increase in the reaction rate was not observed.

Most of the aromatic compounds enumerated above have already been subjected to alkylation in the presence of aluminum chloride to yield cyclohexyl derivatives. The following compounds were obtained in this manner: from toluene – p- and m-cyclohexyltoluenes [7-9]; from chlorobenzene and bromobenzene – p-halophenylcyclohexanes [10]; from diphenyl, diphenylmethane, 1,2-diphenylethane and naphthalene, respectively – 4-cyclohexyldiphenyl, 4-cyclohexyldiphenylmethane, 4-cyclohexyldibenzyl and 2-cyclohexylnaphthalene [9]; from p-xylene – 3-cyclohexyl-p-xylene [8]; from m-xylene – 5-cyclohexyl-m-xylene [8, 11]; from anisole – p-cyclohexylanisole [9, 12]; and from phenylcyclohexane – 1,4-dicyclohexylbenzene [13]. All of these reactions give an excellent yield of the final products, which justifies their use for kinetic measurements.

## EXPERIMENTAL RESULTS

The results of the kinetic measurements are given in the following four tables, in which connection for five of the compounds the experiments were run only at one temperature.

For all of the studied aromatic compounds (except anisole) we found the same general rules for the alkylation reaction as had been published by us earlier [5]. The process proved to be monomolecular with respect to the alkyl halide, while a change of only 35-40% in the rate when the aluminum chloride concentration was approximately doubled again confirmed the fractional order of the reaction with respect to the catalyst when it (the reaction) was run in nitrobenzene medium. The solitary exception to this was anisole, for which the calculated alkylation rate constant decreased with time, while the influence of catalyst concentration was even greater than for the other compounds. On the assumption that this depends on the deactivation of the aluminum chloride due to cleavage of the anisole in accord with the reaction $C_6H_5OCH_3 + AlCl_3 \rightarrow C_6H_5OAlCl_2 + CH_3Cl$, we extrapolated the rate constants calculated for it to zero reaction time, which values are given in Table 5.

The obtained results are plotted in Figs. 1 and 2 in the coordinates: logarithm $k_1$ – reciprocal of the temperature. Although for some of the compounds the measurements were made only at three temperatures and the

TABLE 1

Homologs of Benzene

| Temperature | Aluminum chloride conc. (in mole/min.) | Number of parallel expts. | Average error (in %) | Rate constant $k_2$ (liter/mole/min.) |
|---|---|---|---|---|
| Toluene (concentration 1.364M) | | | | |
| 20.0° | 0.203 | 4 | 1.7 | 0.0352 |
| 25.0 | 0.203 | 3 | 1.1 | 0.0615 |
| 30.0 | 0.203 | 6 | 2.1 | 0.102 |
| 30.0 | 0.049 | 3 | 1.3 | 0.0485 |
| 35.0 | 0.049 | 3 | 1.3 | 0.078 |
| 40.0 | 0.049 | 4 | 1.9 | 0.123 |
| Ethylbenzene (concentration 1.347M) | | | | |
| 20.0 | 0.100 | 3 | 0.9 | 0.0243 |
| 25.0 | 0.100 | 3 | 1.5 | 0.0405 |
| 30.0 | 0.100 | 5 | 2.6 | 0.069 |
| 30.0 | 0.203 | 2 | 0.3 | 0.095 |
| 35.0 | 0.100 | 3 | 1.8 | 0.111 |
| Isopropylbenzene (concentration 1.309M) | | | | |
| 20.0 | 0.100 | 3 | 1.2 | 0.0213 |
| 25.0 | 0.100 | 4 | 2.3 | 0.036 |
| 30.0 | 0.100 | 3 | 1.7 | 0.062 |
| 30.0 | 0.203 | 5 | 2.1 | 0.084 |
| 35.0 | 0.100 | 2 | 0.9 | 0.101 |
| m-Xylene (concentration 1.343M) | | | | |
| 25.0 | 0.203 | 3 | 1.7 | 0.0885 |
| 30.0 | 0.203 | 5 | 2.2 | 0.147 |
| 30.0 | 0.049 | 2 | 1.2 | 0.066 |
| 35.0 | 0.049 | 3 | 1.5 | 0.104 |

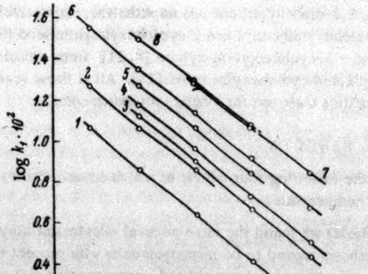


Fig. 1. Rate of alkylation as a function of the temperature for aromatic hydrocarbons. 1) Diphenyl, 2) 1,2-diphenylethane, 3) isopropylbenzene, 4) ethylbenzene, 5) diphenylmethane, 6) toluene, 7) naphthalene, 8) m-xylene.

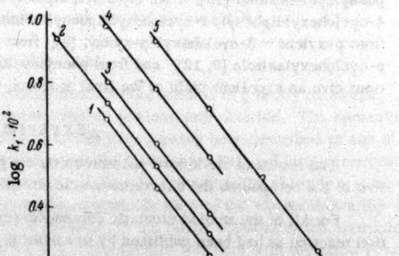


Fig. 2. Rate of alkylation as a function of the temperature for halo derivatives of benzene and toluene. 1) Bromobenzene, 2) chlorobenzene, 3) p-chlorotoluene, 4) o- and m-chlorotoluenes, 5) fluorobenzene.

### TABLE 2

Halo Derivatives of Benzene and Toluene (concentration of aluminum chloride 0.203 M)

| Temperature | No. of parallel expts. | Average error (in %) | Rate constant $k_2$ (liter/mole/min.) |
|---|---|---|---|
| | Fluorobenzene (1.397M) | | |
| 30.0 | 4 | 1.4 | 0.0129 |
| 35.0 | 3 | 2.3 | 0.0225 |
| 40.0 | 5 | 1.7 | 0.0375 |
| 45.0 | 4 | 1.2 | 0.0615 |
| | Chlorobenzene (1.380M) | | |
| 40.0 | 6 | 1.3 | 0.0151 |
| 45.0 | 3 | 0.9 | 0.0249 |
| 50.0 | 4 | 2.2 | 0.039 |
| 55.0 | 3 | 1.6 | 0.063 |
| | Bromobenzene (1.377M) | | |
| 40.0 | 5 | 1.5 | 0.0128 |
| 45.0 | 3 | 2.9 | 0.021 |
| 50.0 | 4 | 3.4 | 0.035 |
| | o-Chlorotoluene (1.352M) | | |
| 40.0 | 4 | 0.9 | 0.0268 |
| 45.0 | 3 | 1.7 | 0.0445 |
| 50.0 | 4 | 2.2 | 0.071 |
| | m-Chlorotoluene (1.352M) | | |
| 40.0 | 4 | 0.9 | 0.0272 |
| 45.0 | 2 | 1.3 | 0.045 |
| 50.0 | 3 | 1.5 | 0.0525 |
| | p-Chlorotoluene (1.352M) | | |
| 40.0 | 5 | 1.8 | 0.0177 |
| 45.0 | 3 | 0.9 | 0.0297 |
| 50.0 | 4 | 1.6 | 0.047 |

activation energies were calculated analytically, the data for them are also shown in the given graphs, in order to illustrate the degree of accuracy of the found constants and their agreement with the Arrhenius rule. In plotting the measurement results for toluene and m-xylene, in order to reduce them to the same catalyst concentration, we took as a base the rate constant at the lowest temperature, from which by means of the temperature coefficient of the rate, found for another catalyst concentration, the constants for other temperatures were calculated.

## DISCUSSION OF RESULTS

The relative rates of alkylation were calculated as a ratio of the constants obtained for the given compound and benzene (at 30° and an aluminum chloride concentration of 0.203 M). The corresponding values for benzene were taken from our previous study [5]. For the halo derivatives of benzene and toluene the reactivities were compared at 40° and the same catalyst concentration, basing the calculations on the fluorobenzene, for which data exist at both 30 and 40°.

TABLE 3

Binuclear Aromatic Hydrocarbons

| Temperature | Aluminum Chloride conc. (in mole/liter) | Number of parallel expts. | Average error (in %) | Rate constant $k_2$ (liter/mole/min.) |
|---|---|---|---|---|
| Diphenyl (concentration 1.323M) | | | | |
| 25.0 | 0.049 | 3 | 1.3 | 0.0199 |
| 30.0 | 0.049 | 3 | 1.3 | 0.0335 |
| 30.0 | 0.203 | 4 | 1.2 | 0.074 |
| 35.0 | 0.049 | 3 | 1.6 | 0.055 |
| 40.0 | 0.049 | 4 | 3.1 | 0.088 |
| Diphenylmethane (concentration 1.263M) | | | | |
| 25.0 | 0.203 | 3 | 1.5 | 0.056 |
| 30.0 | 0.203 | 4 | 1.7 | 0.092 |
| 35.0 | 0.203 | 4 | 1.9 | 0.148 |
| 1,2-Diphenylethane (concentration 1.239M) | | | | |
| 30.0 | 0.049 | 4 | 1.6 | 0.058 |
| 30.0 | 0.203 | 5 | 2.2 | 0.125 |
| 35.0 | 0.049 | 3 | 2.1 | 0.093 |
| 40.0 | 0.049 | 4 | 2.1 | 0.142 |
| Naphthalene (concentration 1.361M) | | | | |
| 20.0 | 0.203 | 3 | 1.7 | 0.052 |
| 25.0 | 0.203 | 3 | 2.2 | 0.088 |
| 30.0 | 0.203 | 4 | 1.7 | 0.143 |

TABLE 4

Temperature 30.0°, $AlCl_3$ concentration 0.203 M

| Expt. Nos. | Aromatic compound | Hydrocarbon concentration | Number of parallel expts. | Average error (in %) | Rate constant $k_2$ (liter/mole/min.) |
|---|---|---|---|---|---|
| 1 | Butylbenzene (sec). . . . . . . . | 1.283 | 4 | 1.9 | 0.077 |
| 2 | Butylbenzene (tert) . . . . . . . | 1.292 | 3 | 0.9 | 0.066 |
| 3 | Phenylcyclohexane . . . . . . . | 1.373 | 3 | 1.4 | 0.083 |
| 4 | p-Xylene. . . . . . . . . . . . . | 1.337 | 5 | 2.2 | 0.125 |
| 5 | 1,4-Diphenylbutane . . . . . . . | 1.213 | 4 | 1.8 | 0.128 |

TABLE 5

Anisole (concentration 1.367 M)

| Temperature | Aluminum chloride conc. (in M) | Number of parallel expts. | Average error (in %) | Rate constant (liter/mole/min.) |
|---|---|---|---|---|
| 30.0° | 0.203 | 4 | 4 | 0.058 |
| 30.0 | 0.100 | 3 | 3 | 0.031 |
| 35.0 | 0.100 | 3 | 4 | 0.047 |
| 40.0 | 0.100 | 3 | 5 | 0.075 |

## TABLE 6

Reactivity of Aromatic Compounds

| Expt. Nos. | Aromatic compound | Relative reaction rate | Energy of activation (kcal./gram-mole) |
|---|---|---|---|
| 1 | Benzene [5] . . . . . . . . | 1.00 | 18.7 ± 0.8 |
| 2 | Toluene . . . . . . . . . . | 2.24 | 18.2 ± 0.5 |
| 3 | Ethylbenzene . . . . . . . | 2.09 | 18.1 ± 0.5 |
| 4 | Isopropylbenzene. . . . . | 1.85 | 18.4 ± 0.5 |
| 5 | sec-Butylbenzene . . . . | 1.69 | — |
| 6 | tert-Butylbenzene . . . . | 1.45 | — |
| 7 | Phenylcyclohexane . . . | 1.82 | — |
| 8 | m-Xylene . . . . . . . . . | 3.23 | 17.3 ± 0.7 |
| 9 | p-Xylene. . . . . . . . . . | 2.74 | — |
| 10 | Diphenyl. . . . . . . . . . | 1.63 | 18.4 ± 0.3 |
| 11 | Diphenylmethane . . . . | 2.02 | 17.8 ± 0.3 |
| 12 | 1,2-Diphenylethane. . . | 2.75 | 17.7 ± 0.3 |
| 13 | 1,4-Diphenylbutane. . . | 2.81 | — |
| 14 | Naphthalene. . . . . . . . | 3.14 | 17.8 ± 0.4 |
| 15 | Fluorobenzene . . . . . . | 0.283 | 19.9 ± 0.4 |
| 16 | Chlorobenzene . . . . . . | 0.114 | 19.5 ± 0.5 |
| 17 | Bromobenzene . . . . . . | 0.097 | 20.1 ± 0.4 |
| 18 | o-Chlorotoluene . . . . . | 0.202 | 19.7 ± 0.4 |
| 19 | m-Chlorotoluene. . . . . | 0.205 | 19.6 ± 0.5 |
| 20 | p-Chlorotoluene . . . . . | 0.134 | 19.5 ± 0.9 |
| 21 | Anisole. . . . . . . . . . . | 1.27 | 17 ± 1.3 |

**The relative reaction rates and calculated activation energies are summarized in Table 6.**

**Plotting the obtained results in the coordinates: logarithm of the relative reaction rate (R) – energy of activation (Fig. 3), reveals that a linear relationship exists between these values. Anisole was the single major exception to this, the data for which are in general the least accurate. For all of the other compounds the deviations of the activation energies from a straight line do not exceed 300-400 cal., which is within the limits of possible error in their determinations.**

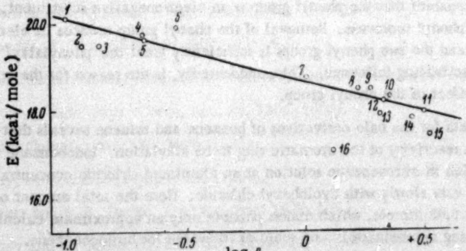


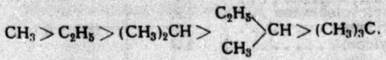
Fig. 3. Reactivity of aromatic compounds as a function of the energy of activation. 1) $C_6H_5Br$, 2) $C_6H_5Cl$, 3) n-$ClC_4H_4CH_3$, 4) o-$ClC_6H_4CH_3$, 5) m-$ClC_6H_4CH_3$, 6) $C_6H_5F$, 7) $C_6H_6$, 8) diphenyl, 9) $C_6H_5CH(CH_3)_2$, 10) $C_6H_5CH_3$, 11) $C_{10}H_8$, 12) $C_6H_5C_2H_5$, 13) $(C_6H_5)_2CH_2$, 14) dibenzyl, 15) m-xylene, 16) anisole.

The presence of the given linear relationship indicates that in the reaction rate equation:

$$k_2 = PZ \cdot e^{-\frac{E}{RT}},$$

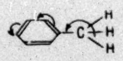
the factor PZ is a constant for all of the studied compounds, and that differences in the alkylation rate of aromatic compounds depend only on variations in the activation energies. Similar relationships in substitutions in the aromatic ring were also observed for some other cases [14], which permits stating that this rule is quite general for reactions of this type.

As can be seen from the data in the preceding table, the introduction of one, or even more so, of two alkyl groups into the aromatic ring increases its reactivity, which in general is characteristic for electrophilic substitution reactions of aromatic compounds. Here either a lengthening or branching of the alkyl group causes a reduction in its activating action:



$$CH_3 > C_2H_5 > (CH_3)_2CH > \begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!CH > (CH_3)_3C.$$

A similar influence of the structure of the alkyl group was observed in the chlorination [15] and bromination [16] of aromatic compounds, and also in the experiments of Condon [3] when he alkylated benzene with propylene. The latter author ascribes the given phenomenon as due to ortho-substitution steric hindrance. However, to us it seems more valid to attribute it to the $\sigma - \pi$ conjugation effect.



In comparison to other substitution reactions in the aromatic ring, alkylation by the Friedel-Crafts method is characterized by a weak influence of the alkyl group on the reactivity. Thus, the rate for the bromination of toluene when compared with benzene is 467 [17], for chlorination it is 353 [15], for nitration it is 23 [18], for acetylation in the presence of aluminum chloride it is 13.3 [19], for sulfonation it is 5.1 [20], while for alkylation, according to our data, it is equal to 2.24, according to Condon it is equal to 2.1 [3], and according to Brown and Grayson it is equal to 1.64 [4]. Such a marked variation must be due to polarization effects, arising under the influence of the electrophilic reagents attacking the molecule, which possess a variable positive charge. Such a viewpoint also makes it possible to understand the differences in the figures given for the alkylation reaction, since these figures were obtained with alkylating agents of different activity.

For binuclear aromatic compounds of the type of diphenyl and diphenylalkanes the reactivity increases with increase in the distance between the two aromatic rings. When compared with benzene homologs, these compounds possess twice as many active centers at which substitution can occur. Consequently, to find the actual degree of activation of each of their benzene rings it is necessary to divide the figures, given for them in Table 3, in half. Then it becomes apparent that the phenyl group is an electronegative substituent, deactivating the second benzene ring in the diphenyl molecule. Removal of the phenyl group reduces its electronegative action, and when the distance between the two phenyl groups is sufficiently great the phenylalkyl group begins to approximate an alkyl group in its activating influence. This, undoubtedly, is the reason for the gradual damping of the electronegative induction effect of the phenyl group.

Examination of the data for the halo derivatives of benzene and toluene reveals that the introduction of a halogen atom decreases the reactivity of the aromatic ring in its alkylation. Iodobenzene proved to be especially inactive in this respect, which in nitrobenzene solution at an aluminum chloride concentration of 0.203 M and a temperature of 40° reacts very slowly with cyclohexyl chloride. Here the total amount of hydrogen chloride evolved in 5 min was about 0.03 mmole, which makes possible only an approximate calculation of the rate constant ($k_1 = 0.002 \text{ min}^{-1}$), being approximately one tenth of the value for bromobenzene.

Consequently, in their deactivating action on the benzene ring in its alkylation the halogen substituents fall into the following order: $I \gg Br > Cl \gg F \gg H$.

A similar regular order of their arrangement, reverse to the change in the induction effect, depends, apparently, on the conjugation. It should be mentioned that Ingold and Smith [21] disclosed a different sequence in the case of nitration: $Br > Cl > I \approx F > H$.

The deactivating influence exerted by halogen atoms during alkylation in the presence of aluminum chloride proved to be nearly the same as in chlorination [22], but much smaller than in the case of nitration [21]. According to the data of Brown and Grayson, the relative rate for the alkylation of chlorobenzene is much higher than the value obtained by us (0.47 instead of 0.114). This also possibly depends on the differences in the activity of the alkylating agents.

The deactivating influence exerted by halogen substituents on the aromatic ring greatly exceeds the activating influence exerted by alkyl groups, which can be clearly seen from the example of the chlorotoluenes, which react more slowly than does benzene. Of the chlorotoluenes the least reactive proved to be the para-isomer, in which the orienting influence exerted by the substituents is opposed to each other. Regarded from this viewpoint it seems somewhat strange that the m- and o-chlorotoluenes have nearly the same activity. A probable explanation for this is the factor of steric hindrance when the meta-isomer is alkylated in the ortho-position to the substituents already present, which is not the case for o-chlorotoluene.

In combination with the data for the p- and m-xylenes it becomes possible to give the following order for variation in the reactivities of disubstituted benzene derivatives: meta > ortho > para.

The obtained results give a fairly complete picture of the influence exerted by substituents on the reactivity of aromatic compounds when alkylated in the presence of aluminum chloride, which also permits predicting to some degree the results for other compounds.

## SUMMARY

1. The reactivity of 21 aromatic compounds was studied when they were alkylated with cyclohexyl chloride in the presence of aluminum chloride, and the energies of activation were determined for 15 of them.

2. The influence of various structural factors on this reaction was shown, including the structure of the alkyl group, the nature of the halogen atoms, the position of a phenyl substituent in the side chain, and others.

3. It was shown that differences in the reactivities of aromatic compounds when alkylated depend only on variations in the energies of activation, with the PZ factor of the rate equation remaining constant.

## LITERATURE CITED

[1] S. C. J. Olivier and G. Berger, Rec. trav. chim. 45, 710 (1926).

[2] A. W. Francis and E. E. Reid, Ind. Eng. Chem. 38, 1194 (1946).

[3] F. E. Condon, J. Am. Chem. Soc. 70, 2265 (1948).

[4] H. C. Brown and M. Grayson, J. Am. Chem. Soc. 75, 6285 (1953).

[5] N. N. Lebedev, J. Gen. Chem. 24, 664 (1954).*

[6] K. Weigand, Experimental Methods in Organic Chemistry, Part 1 (1951).**

[7] N. Kursanov, J. Russ. Phys.-Chem. Soc. 38, 1304 (1906).

[8] D. Bodroux, Compt. rend. 186, 1005 (1928).

[9] D. Bodroux, Ann. chim. (10), 11, 511 (1929).

[10] H. A. Mayes and E. E. Turner, J. Chem. Soc. 1929, 500.

[11] M. Battegay and M. Kappeler, Bull. Soc. Chim. (4) 35, 989 (1924).

[12] J. F. Bartlett and C. E. Garland, J. Am. Chem. Soc. 49, 2098 (1927).

[13] J. v. Braun, Ber. 60, 1180 (1927).

[14] S. C. Hinshelwood, Trans. Faraday Soc. 34, 138 (1933); L. P. Hammet, Physical Organic Chemistry, New York (1940).

[15] P. B. D. de la Mare and P. W. Robertson, J. Chem. Soc. 1943, 279.

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* Original Russian pagination. See C.B. Translation.

** In Russian.

[16] E. Berliner and F. Berliner, J. Am. Chem. Soc. 7, 222 (1950).

[17] E. Berliner and F. J. Bondhus, J. Am. Chem. Soc. 68, 2355 (1946).

[18] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, J. Chem. Soc. 1931, 1959.

[19] H. F. McDuffie and G. Dougherty, J. Am. Chem. Soc. 64, 297 (1942).

[20] F. J. Stubbs, C. D. Williams, and C. N. Hinshelwood, J. Chem. Soc. 1948, 1065.

[21] C. K. Ingold and M. S. Smith, J. Chem. Soc. 1938, 905.

[22] F. Bourion, Ann. chim. 14, 215 (1920).

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# POISONING ACTION OF SOME SILANES ON PLATINUM CATALYST

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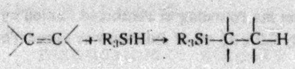
The first to observe the poisoning of a platinum catalyst were Dobereiner and Faraday [1] more than a hundred years ago, and in this case sulfur compounds proved to be the reason for the poisoning. As regards organosilicon compounds, the following cases of their poisoning metallic catalysts are known: dimethylsiloxane vapors prevent the reaction of hydrogen with oxygen on a platinum catalyst [2], while triphenylsilanol cannot be hydrogenated over nickel oxide [3]. However, A. D. Petrov and S. I. Sadykh-zade [4] were able to hydrogenate, both completely and partially, silicohydrocarbons, containing double and triple bonds, in the presence of palladium oxide deposited on calcium carbonate. It is also known that platinum black or platinum on asbestos or on silica gel are catalysts for the addition of organosilicon compounds, containing the Si–H bond, to the double bond of olefins [5]:



$$>C=C< + R_3SiH \rightarrow R_3Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

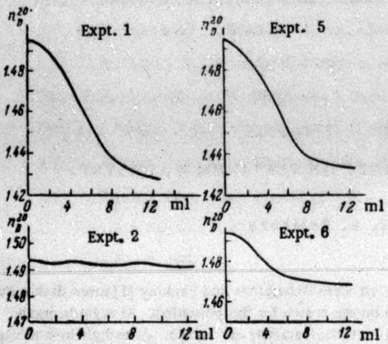
Attempts to obtain compounds with a silicon atom in a ring containing aromatic double bonds, starting with pentamethylenesilane and methylpentamethylenesilane, in the presence of either platinum or palladium catalyst, at temperatures up to 500°, failed to give positive results [6]. Strictly speaking, the data known to us on the reaction of organosilicon compounds with metallic catalysts are limited to the above.

The behavior of six- and five-membered cyclic hydrocarbons in the presence of platinized carbon is well known: six-membered hydrocarbons at 300° are smoothly converted into benzene and its homologs [7], while five-membered hydrocarbons in the presence of hydrogen suffer hydrogenolysis with cleavage of the five-membered ring and are transformed into paraffinic hydrocarbons [8]. It could be assumed that five-membered silicohydrocarbons with one silicon atom in the ring, in the presence of hydrogen, will also suffer hydrogenolysis, but in this case, in contrast to the hydrocarbons, it is possible for rupture to occur at both the C–C and the Si–C bonds. However, it was shown experimentally that cyclic silicohydrocarbons behave differently in the presence of platinized carbon than do the cyclic hydrocarbons.

When we attempted, in the presence of platinized carbon at 300°, the hydrogenolysis of the five-membered silicohydrocarbon – dimethyltetramethylenesilane – and the six-membered silicohydrocarbon – dimethylpentamethylenesilane – we found that these compounds act as selective poisons for platinum catalyst. Such an observation merited a more detailed study, since the use of selectively acting poisons can be of some practical interest, while examples of the selective poisoning of catalysts are not too numerous.

## EXPERIMENTAL

The preparation of the dimethyltetramethylenesilane and dimethylpentamethylenesilane has been described earlier [9, 10]. Tetraethylsilane was obtained by the reaction of ethylmagnesium bromide with silicon tetrachloride. The properties of the starting silicohydrocarbons were: dimethyltetramethylenesilane, b. p. 106.0-106.1° at 760 mm, $n_D^{20}$ 1.43487, $d_4^{20}$ 0.7938; m. p. −92°; dimethylpentamethylenesilane: b. p. 131.2-131.3° at 740 mm, $n_D^{20}$ 1.4428, $d_4^{20}$ 0.8111; tetraethylsilane, b. p. 152.0-152.2° at 758 mm, $n_D^{20}$ 1.4265.

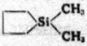
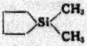
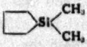
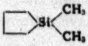
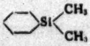


Poisoning action of silanes on platinum catalyst. Experimental conditions are given in the table and text.

The catalyst – platinized carbon (15% Pt) – was prepared by the method of [11]. The catalyst, in an amount of either 5 or 10 ml (either 1.5 or 3 g), was placed in a glass tube with a diameter of 10 mm, heated in a tube furnace with temperature control, and reduced in a stream of hydrogen at 300-320° for 1 hr. The hydrogen was obtained by electrolysis. To determine the activity of the catalyst we passed cyclohexane (b. p. 80.4-80.5° at 750 mm, $n_D^{20}$ 1.4262) over it for 2 hrs at 300° and a space velocity of 0.32; the catalyzate had $n_D^{20}$ 1.4942, i. e., it contained 94% benzene. Each experiment was run with a fresh portion of catalyst, having the activity indicated above. A uniform liquid-feed piston pump [12] was used to feed the silicohydrocarbon or its solution in cyclohexane into the tube. The space velocity in all of the experiments was 0.30-0.32.

Experiments with dimethyltetramethylenesilane. Dimethyltetramethylenesilane (9.7 g) (0.08 mole) was passed over 10 ml (3 g) of platinized carbon (15% Pt) in a stream of hydrogen at 300°. The catalyzate (9.3 g) had b. p. 104-105° at 750 mm and $n_D^{20}$ 1.4347, i. e., it represented the starting silane.

Results of Experiments on the Poisoning of Platinized Carbon by Silanes in Cyclohexane Solution (Space Velocity 0.32; 13 ml of Solution was Passed Through in Each Experiment)

| Expt. No. | Formula of silane | Concentration (vol. %) | Expt. temperature | $n_D^{20}$ of catalyzate at end of expt. | % conversion of $C_6H_{12}$ into $C_6H_6$ at 300° at end of expt. |
|---|---|---|---|---|---|
| 1 |  | 1 | 300 | 1.4261 | 0 |
| 2 |  | 0.1 | 300 | 1.4907 | 91 |
| 3 |  | 1 | 250 | 1.4440 | 31 |
| 4 |  | 1 | 200 | 1.4658 | 59 |
| 5 |  | 1 | 300 | 1.4315 | 9 |
| 6 | $Si(C_2H_5)_4$ | 1 | 300 | 1.4682 | 63 |

To determine the activity of the catalyst after passing the silane over it we immediately passed cyclohexane over the catalyst at 300° and a space velocity of 0.32. The obtained catalyzate had $n_D^{20}$ 1.4262, i. e., it was the original cyclohexane. Then benzene ($n_D^{20}$ 1.5009) was passed over the catalyst at 180-190° and with the same velocity as before, in a slow stream of hydrogen. The obtained catalyzate had $n_D^{20}$ 1.5009, i. e., the benzene was not hydrogenated under these conditions. When 1-methyl-2-cyclopentene ($n_D^{20}$ 1.4218) was passed over the same catalyst a catalyzate was obtained that failed to decolorize bromine water and had $n_D^{20}$ 1.4100, i. e., it represented the saturated methylcyclopentane.

Experiments with tetraethylsilane. Tetraethylsilane (11.8 g) (0.08 mole) was passed over 10 ml of the catalyst in a stream of hydrogen at 300°. The catalyzate (11.5 g) had $n_D^{20}$ 1.4265, i. e., it represented the unchanged silane. To determine the activity of the catalyst some cyclohexane was passed through it at 300°; the obtained catalyzate had $n_D^{20}$ 1.4420, i. e., it contained ~ 30% benzene.

Experiments with solutions of dimethyltetramethylenesilane, dimethylpentamethylenesilane and tetraethylsilane in cyclohexane. 1% and 0.1% (by volume) solutions of dimethyltetramethylenesilane, dimethylpentamethylenesilane and tetraethylsilane were passed over 5 ml (1.5 g) of platinized carbon at 300, 250 and 200°. Samples of the catalyzate were taken at 15-20 min intervals and its refractive index was determined. The experimental results are given in the table and plotted on the graphs, where the volume of catalyzate taken is plotted in milliliters along the abscissa, while the corresponding index of refraction is plotted along the ordinate. The shape of the curves reflects the loss in catalyst activity relative to the dehydrogenation of cyclohexane. In Expts. 3 and 4, where the poisoning of the catalyst by dimethyltetramethylenesilane solution was done at 200 and 250°, the degree of catalyst poisoning was determined by the subsequent passage of cyclohexane over it at 300°.

Regeneration of poisoned platinized carbon. I. To 10 ml of platinized carbon, completely poisoned after treatment with dimethyltetramethylenesilane, was added 1-2 ml of ethyl alcohol and the latter was ignited. The alcohol burned for several min, and then the carbon continued to glow for another 5-7 min. The Pt-carbon treated in this manner was then reduced in a stream of hydrogen at 300-320°, after which its activity was determined. When cyclohexane was passed over it at 300° and a space velocity of 0.32 a catalyzate was obtained with $n_D^{20}$ 1.4468, containing 35% benzene.

II. Five milliliters of the catalyst, completely poisoned in the same manner as described above, was treated in a lead vessel for 1 hr with hydrogen fluoride vapors, with heating of the vessel on a boiling water bath. After washing with distilled water for 5-6 hrs and drying at 105-110° for 2 hrs the catalyst was reduced in a stream of hydrogen at 300-320°. Passage of cyclohexane over the catalyst at a space velocity of 0.4 gave a catalyzate with $n_D^{20}$ 1.4907, i. e., the amount of benzene in it was 90%.

## DISCUSSION OF RESULTS

From an examination of the obtained data it follows that silicohydrocarbons, both as such and when taken as dilute solutions in cyclohexane, poison platinized carbon relative to the dehydrogenation of cyclohexane and the hydrogenation of benzene. However, here the catalyst retains the ability to hydrogenate the double bond. Cyclic silanes are stronger catalyst poisons than is the acyclic silane – tetraethylsilane. Dimethyltetramethylenesilane, having a five-membered ring, is a somewhat stronger catalyst poison than dimethylpentamethylenesilane, having a six-membered ring in its molecule. To completely poison 5 ml (1.5 g) of 15% Pt-carbon relative to the dehydrogenation of cyclohexane requires the passage of about 13 ml of a 1% (by volume) dimethyltetramethylenesilane solution at 300° and a space velocity of 0.32, i. e., about 0.1 g (0.0088 mole) of the silane is required (figure, Expt. 1). The same amount of a 0.1% solution at the same temperature turns out to be almost without effect as a catalyst poison (Expt. 2).

The higher the experiment temperature (in the interval 200-300°), the more rapidly is the catalyst poisoned. Thus, 13 ml of a 1% dimethyltetramethylenesilane solution at 300° completely poisons 5 ml of the catalyst, while if the same amount of solution is passed through at 250° the catalyst continues to dehydrogenate cyclohexane to the extent of 31%, and if the same experiment is run at 200° – even to the extent of 60%. Such a dependence of catalyst poisoning on the temperature is evidence that apparently the poisoning process is determined not by adsorption of the original silane, but by the blocking of the active centers of the catalyst by its decomposition products. Such a poisoning results not only in the deposition of a carbonaceous film [13] (since as the result of oxidation the activity of the catalyst is only partially restored), but also in the deposition of silicon or its compounds on the catalyst surface, since after treating the poisoned catalyst with hydrogen fluoride the catalyst again displays its original activity.

The fact that a five-membered silane exerts the greatest catalyst-poisoning effect is possibly associated with the strain that is suffered by a five-membered cycle with one silicon atom [14].

Consequently, both cyclic and acyclic silicohydrocarbons are poisons for platinized carbon, but the cyclic members exert a much stronger action. The probable explanation for this is that rupture of the Si–C bond in the presence of Pt-carbon proceeds with greater ease in the case of the cyclic than in the case of the acyclic system. A similar difference in the stability of Si–C bonds was observed by us earlier in the action of concentrated sulfuric acid on various cyclic and acylic silicohydrocarbons [10].

## SUMMARY

1. It was established that very small amounts of silicohydrocarbons, especially the cyclic derivatives, cause the poisoning of platinized carbon relative to the dehydrogenation of cyclohexane and the hydrogenation of benzene, although the catalyst retains the ability to hydrogenate double bonds.

2. The process of poisoning Pt-carbon at various temperatures and concentrations of silicohydrocarbons in cyclohexane solutions was studied.

## LITERATURE CITED

[1] G. M. Schwab, Handbuch der Katalyse, Wien, Springer Verlag, B. VI, 234 (1943).

[2] R. H. Savage, J. Chem. Phys. 16, 237 (1948).

[3] B. N. Dolgov and Yu. N. Volnov, J. Gen. Chem. 1, 91 (1931).

[4] A. D. Petrov, S. I. Sadykh-zade and Yu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1954, 722.*

[5] U. S. Patent 2632013; Ch. A. 48, 2760 (1954); D. L. Bailey and A. N. Pines, Ind. Eng. Chem. 46, 2363 (1954); U. S. Patent 2637738; C. A. 48, 8254 (1954).

[6] R. West, J. Am. Chem. Soc. 77, 2339 (1955).

[7] N. D. Zelinsky, Collected Works (Acad. Sci. USSR Press, 1955), III. **

[8] B. A. Kazansky, Progr. Chem. 17, 641 (1948).

[9] A. F. Plate, N. A. Momma, and Yu. P. Egorov, Proc. Acad. Sci. USSR 97, 874 (1954).

[10] A. F. Plate, N. A. Belikova, and Yu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1085.*

[11] N. D. Zelinsky and M. B. Turova-Polyak; cf.: N. D. Zelinsky, Collected Works (Acad. Sci. USSR Press, 1955), III, 271. **

[12] A. M. Levit and L. Kh. Freidlin, Factory Labs. 16, 244 (1950).

[13] N. D. Zelinsky, Collected Works (Acad. Sci. USSR Press, 1955), III,7.**

[14] A. F. Plate, N. A. Belikova, and Yu. P. Egorov, Proc. Acad. Sci. USSR 102, 1131 (1955).

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** In Russian.

# SYNTHESIS OF ENYNES BY THE METHOD OF EXHAUSTIVE METHYLATION

Ya. M. Slobodin

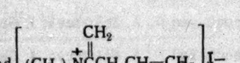
The question of triple bond formation in the thermal decomposition of quaternary ammonium bases represents great interest. The literature on this question is inadequate and somewhat contradictory. We had shown [1] that the decomposition of bis(trimethylammonium)ethane hydroxide gives acetylene in good yield. It was also established by us [2] that the thermal decomposition of 1,2-bis(trimethylammonium)propane hydroxide, 1,3-bis(trimethylammonium)propane hydroxide and trimethylallylammonium hydroxide yields methylacetylene in all cases; in not one of the enumerated cases did the formation of allene occur.

According to the data obtained by Hurd and Drake [3], the decomposition of 1,2-bis(trimethylammonium) butane hydroxide leads to the formation of a mixture of products, containing 44% ethylacetylene and 56% methylallene. Divinyl was not found among the decomposition products by the mentioned authors. The decomposition of 2,3-bis(trimethylammonium)butane hydroxide gave a hydrocarbon mixture, containing 42-47% divinyl. The remainder, in the opinion of the authors, was a mixture of methylallene and dimethylacetylene.

In contradiction to these data we found [4] that the decomposition of 2,3-bis(trimethylammonium)butane hydroxide yields only divinyl. The formation of methylallene, dimethylacetylene and ethylacetylene in noticeable amounts was not observed. Similar results were obtained by Mannich and Margotte in the decomposition of 1,3-bis(trimethylammonium)butane hydroxide, where only divinyl is formed [5]. As a result, the data of Hurd and Drake [3] are not supported. It could be postulated that acetylenes are formed in the decomposition of only such bis-ammonium bases as contain not more than three carbons in the hydrocarbon chain. When four and more carbon atoms are present in the hydrocarbon chain then only such hydrocarbons are formed as contain a conjugated system of double bonds. Independent of the number of carbon atoms the formation of allenes does not occur.

The possibility of obtaining hydrocarbons, containing a conjugated system of ethylene-acetylenic bonds in a chain with four or more carbon atoms, by the method of exhaustive methylation is also quite obscure. It could be postulated that enynes will be obtained both in the thermal decomposition of hydroxides, containing one ammonium group and two double bonds, and in the decomposition of hydroxides, containing two quaternary ammonium groups and one double bond. Compounds belonging to the first type include:

$[(CH_3)_3\overset{+}{N}CH_2CH_2CH{=}C{=}CH_2]I^-$ and



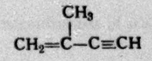
$$\left[(CH_3)_3\overset{+}{N}\overset{\overset{\large CH_2}{\|}}{C}CH_2CH{=}CH_2\right]I^-,$$

which were first obtained by Ladenburg, and then by von Braun and Teuffert [6]. The authors assigned the wrong structure to both the intermediate products and the final hydrocarbon, which was later rectified in our study [7], where it was shown that the final product is the enyne – 1-penten-3-yne (pyrylene).

Of the compounds belonging to the second type, only 1,4-bis(trimethylammonium)-2-butene hydroxide [8] and 2,5-bis(trimethylammonium)-3-hexene hydroxide [1] have been studied. When heated in a vacuum (13 mm) the first of these hydroxides gave vinylacetylene in comparatively low yield (about 29%). We ran some experiments on the decomposition of this hydroxide at atmospheric pressure. Here we obtained only traces of vinylacetylene. When decomposed at atmospheric pressure the second of the mentioned hydroxides gave 2-hexen-4-yne in 85% yield.

In addition to this, we give in the present communication the data obtained for the thermal decomposition of 1,4-bis(trimethylammonium)-2-pentene hydroxide and 1,4-bis(trimethylammonium)-2-methyl-2-butene hydroxide. In its decomposition the first of these bases can form two hydrocarbons with a conjugated system of acetylene-ethylenic bonds, (I) and (II). The second base can form only one hydrocarbon (III).

$CH_3-C\equiv C-CH=CH_2$ (I) $CH_3CH=CH-C\equiv CH$ (II)



$$CH_2=\overset{\overset{CH_3}{|}}{C}-C\equiv CH$$ (III)

The distillation of 1,4-bis(trimethylammonium)-2-pentene bromide with 40% caustic solution gave a 40% yield of a hydrocarbon, which had the following properties:

B. p. 58-59°, $d_4^{20}$ 0.7390, $n_D^{20}$ 1.4574. Found %: C 90.72; H 8.75. $C_5H_8$. Calculated %: C 90.91; H 9.09.

The hydrocarbon is unstable and when stored for 4 months it showed 30% polymerization. It reacts partially with an ammoniacal solution of silver oxide. One gram of the hydrocarbon gave 0.04 g of the silver derivative, which calculates as 1.4% of the α-acetylenic hydrocarbon. The Raman spectrum of the hydrocarbon was found to contain the following group of frequencies $\nu$(in $cm^{-1}$): 1590, 1605, 1618, 1936, 2046, 2102, 2245, which support its structure as being a conjugated enyne.

As a result, it was established that the distillation of 1,4-bis(trimethylammonium)-2-pentene bromide with caustic yields a mixture of hydrocarbons, containing chiefly 1-penten-3-yne. Its isomer – 3-penten-1-yne – is formed in limited amount. When 1,4-bis(trimethylammonium)-2-methyl-2-butene hydroxide was subjected to thermal decomposition the yields of hydrocarbon were exceedingly small. A large amount of polymeric forms remained in the distillation flask. A comparison of the yields of various enynes obtained by the Hofmann reaction reveals that these hydrocarbons are formed in good yields in those cases where the acetylenic bond is not found at the end of the chain. It is possible that this is associated with the great tendency shown by enynes with an α-acetylenic bond to polymerize.

## SUMMARY

1. It was shown that the thermal decomposition of 1,4-bis(trimethylammonium)-2-pentene hydroxide yields a mixture of enynes, in which 1-penten-3-yne predominates. Its isomer – 3-penten-1-yne – is formed in limited amount.

2. The yields of enyne are exceedingly small in the thermal decomposition of 1,4-bis(trimethylammonium)-2-methyl-2-butene hydroxide.

3. It was observed that enynes are formed in good yields in the thermal decomposition of the corresponding unsaturated bis-ammonium bases in those cases where the acetylenic bond is not found at the end of the chain.

## LITERATURE CITED

[1] Ya. M. Slobodin and N. A. Selezneva, J. Gen. Chem. 26, 691 (1956).*

[2] Ya. M. Slobodin and N. A. Selezneva, J. Gen. Chem. 26, 694 (1956).*

[3] C. Hurd and L. Drake, J. Am. Chem. Soc. 61, 1943 (1939).

[4] Ya. M. Slobodin and O. Sergeev, J. Gen. Chem. 27, 1892 (1957).*

[5] C. Mannich and E. Margotte, Ber. 68, 273 (1935).

[6] Ladenburg, Lieb. Ann. 247, 50 (1886); von Braun and Teuffert, Ber. 61, 1092 (1928).

[7] Ya. M. Slobodin and N. M. Khokhlacheva, J. Gen. Chem. 23, 164 (1953).*

[8] R. Willstätter and T. Wirth, Ber. 46, 538 (1913).

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* Original Russian pagination. See C.B. Translation.

# SYNTHESIS OF ORGANOSILICON COMPOUNDS

## II. COMPARATIVE ACTIVITY OF VARIOUS TYPES OF CONTACT MASSES USED FOR THE SYNTHESIS OF METHYLCHLOROSILANES

V. S. Fikhtengolts and A. L. Klebansky

The x-ray structure analysis of contact masses, used for the synthesis of methylchlorosilanes, permitted us to establish that copper shows transition into an intermetallic compound with silicon [1]. The mechanism proposed by us for the direct synthesis reaction is based on a reduction in the energy of dissociation of the methyl chloride adsorbed on the surface of the contact mass under the influence of the ionized intermetallic compound, which is first of all expressed in a reduction of the temperature for the process.

The main product of the reaction of methyl chloride with silicon is dimethyldichlorosilane, an exceedingly valuable industrial product, since it serves as the starting monomer for the preparation of dimethylpolysiloxane rubber. The other products of the reaction are formed as the result of various side reactions, proceeding concurrently with the main reaction, in which connection the relative ratio of the side reactions in the general process increases with increase in the temperature [2].

As a result, the temperature at which methyl chloride begins to react with silicon, and the related amount of dimethyldichlorosilane which is contained in the condensate, can serve as criteria of the activity of a contact mass. On the basis of the proposed mechanism for the reaction it can be expected that the most active will prove to be those contact masses in which the most complete transition of copper into the intermetallic compound is observed.

TABLE 1

Comparison of the Efficiency of Various Contact Masses*

| Expt No. | Contact mass | Initial expt. temp. | Time of contact (in sec.) | Silicon utilization (in %) | Degree of conversion (in %) | Yield | |
|---|---|---|---|---|---|---|---|
| | | | | | | Condensate from 100 g contact mass (g/hour) | based on reacted silicon (in %) |
| 1 | Powdered alloy ........ | 335° | 3.5 | 52 | 37 | 9.8 | 44 |
| 2 | Briquets of elemental Si and Cu ..... | 335 | 34 | 35 | 64.5 | 5.6 | 36 |
| 3 | Briquets with chemically precipitated Cu | 300 | 26 | 49 | 79 | 8.8 | 39 |
| 4 | The same ....... | 265 | 23 | 76.5 | 64 | 11.1 | 43.5 |

* Expts. 1-3 were run in an electric furnace, and Expt. 4 was run in a saltpeter bath.

The relative activity of different contact masses was compared by the method of running control experiments, with a painstaking study of the reaction products and obtaining a material balance for the experiment. By means of a number of preliminary experiments it was established that the purity of its components was of importance to a contact mass. Consequently, in preparing the contact masses we used either Kr-0 (99.5% Si) or

Kr-1 (99.0% Si) silicon, electrolytic copper powder and chemically pure cuprous chloride, prepared by us by the method of [3], which after preparation was vacuum-dried.

The first experiments on the preparation of methylchlorosilanes were run in a glass tube, heated in an electric furnace; however, when we started to use active contact masses it was found that the direct synthesis reaction has an exothermic character. As a result of this we frequently observed self-heating of the contact mass during experiment with a very substantial temperature rise in the reaction zone. In order to facilitate the removal of excess heat during reaction we used a copper apparatus, placed in a bath containing a melt composed of equimolar amounts of $KNO_3$ and $NaNO_3$ and having m. p. 220°. When the experiments were run under these conditions the reaction temperature proved to be 30-50° lower than when run in a tube furnace.

The most complete transition of copper into intermetallic compound was observed for the alloy of silicon with copper (20%). To avoid oxidation of the copper the fusions were run in a nitrogen atmosphere. However, due to its lack of porosity the alloy has a very small active surface, as a result of which the yield of dimethyldichlorosilane was low, and the utilization of silicon was only 5-10%. Completely satisfactory results were obtained only when the alloy was crushed into particles with a size not exceeding 0.3 mm (Table 1). It is possible to assume that grinding the alloy to a dustlike state and running the process under conditions that would assure good mixing of the methyl chloride with the dustlike contact mass could lead to a further improvement in the results.

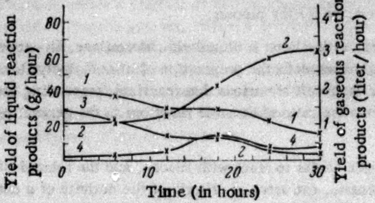

Fig. 1. Variation in the yields of reaction products in the synthesis of methylchlorosilanes. 1) Condensate, 2) gaseous products, 3) dimethyldichlorosilane, 4) methyltrichlorosilane.

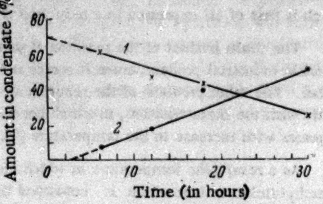

Fig. 2. Change in the composition of the condensate in the synthesis of methylchlorosilanes. 1) dimethyldichlorosilane, 2) methyltrichlorosilane.

The least transition of copper into intermetallic compound was observed for the contact mass that was obtained by the pressing into pellets of powdered silicon and copper (20%), with subsequent baking of the pellets in either a nitrogen or hydrogen atmosphere at 800°. The high temperature, required for the conversion of the copper into intermetallic compound, was responsible for its low degree of dispersion. The experiments run with this contact mass gave less satisfactory (Table 1) and poorly reproducible results. The contact mass, seemingly prepared under constant conditions, frequently differed in its activity. This is apparently due to a large variety of factors, affecting the quality of the contact mass: the size of the copper and silicon particles, the uniformity of their mixing, the conditions of molding and baking, etc. The best results were obtained with a contact mass containing chemically precipitated copper, which not only showed a comparatively complete transition of copper into intermetallic compound, but also a highly developed active surface. This contact mass was prepared by the pressure-molding of a mixture of powdered silicon and cuprous chloride. The heating of these briquets in the reaction apparatus to 260-280° resulted in the distillation of $SiCl_4$ and the separation of metallic copper (20%). The copper, separating in the atomic state, is more active and forms the intermetallic compound even at the above indicated temperature. In addition, due to their high mobility the copper atoms are distributed more uniformly on the silicon surface, which together with the high activity, also assures a good reproducibility of the results obtained with this contact mass.

In contrast to the usual contact-catalytic reactions, where the catalyst shows slight chemical change during the process, the direct synthesis reaction proceeds with a continuous consumption of one of the components of the contact mass. In connection with this the relative amount of the second component, playing the role of catalyst, shows a corresponding increase. A change in the composition of the contact mass causes its activity to change, which in turn should be reflected in a change in the composition of the reaction products during the reaction process.

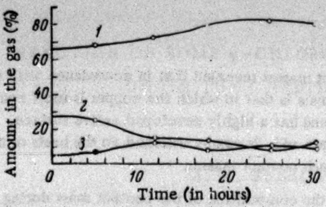

Fig. 3. Change in the composition of gaseous reaction products in the synthesis of methylchlorosilanes. 1) Methane, 2) hydrogen, 3) ethylene.

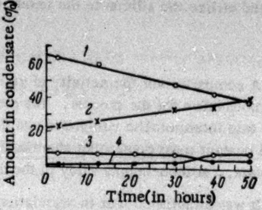

Fig. 4. Change in the composition of the condensate in the synthesis of methylchlorosilanes. 1) $(CH_3)_2SiCl_2$, 2) $CH_3SiCl_3$, 3) $(CH_3)_3SiCl$, 4) $CH_3SiHCl_2$.

TABLE 2

Composition of the Condensates Obtained When Using Different Fillers

| Filler material | Composition of the condensate (in %) | | | | |
|---|---|---|---|---|---|
| | $CH_3SiHCl_2$ | $(CH_3)_3SiCl$ | $CH_3SiCl_3$ | $(CH_3)_2SiCl_2$ | remainder |
| No filler | 4 | 7 | 35 | 45 | 9 |
| Porcelain | 7.8 | 7.2 | 29.4 | 51.2 | 4.4 |
| Magnesium | 7.2 | 5.4 | 29.6 | 50.5 | 7.3 |
| Zinc | 6.1 | 3.8 | 26.0 | 56.8 | 7.3 |
| Brass | 6.9 | 4.8 | 23.7 | 58.0 | 6.6 |

As a result of the performed experiments it was established that during the course of reaction the yield of dimethyldichlorosilane and of the condensate itself decreases, while the yield of methyltrichlorosilane and of the gaseous reaction products increases (Fig. 1). Corresponding to this the composition of the condensate also changes (Fig. 2). The simultaneously occurring changes in the composition of the gaseous reaction products are shown in Fig. 3. In order to maintain the productivity of the contact mass at a sufficiently high level it becomes necessary to gradually raise the temperature in the reaction zone during the course of the process. More detailed changes of the condensate composition in the experiment where a contact mass containing chemically precipitated copper was used are shown in Fig. 4. Figures 1-3 relate to the experiment where the contact mass was composed of elemental silicon and copper.

In order to improve the heat-exchange and the distribution of methyl chloride in the contact mass we mixed various additives with the latter: porcelain and metal turnings. The latter favored an increase in the amount of dimethyldichlorosilane in the condensate also as the result of combining with the excess chlorine atoms. From a number of materials tested as fillers the best results were obtained with brass turnings (Table 2).

An improvement in the composition of the condensate is also achieved by changing the direction of gas flow in the reactor, thus causing a temporary increase in the yield of dimethyldichlorosilane. Thus, for example, in one of the experiments the content of dimethyldichlorosilane in the condensate as the result of changing the direction of methyl chloride addition increased from 43.5 to 61%, while in another experiment it increased from 53 to 68%. A corresponding decrease in the methyltrichlorosilane content occurs simultaneously with this. This phenomenon is explained by the nonuniform utilization of the contact mass during passage of the methyl chloride.

When the direction of adding the methyl chloride is changed it falls on a still comparatively fresh contact mass. A temporary increase in the dimethyldichlorosilane yield occurs as a result of this; after 1 to 2 hrs the yield again drops to its former level. As a result, by running the process under conditions assuring an efficient removal of heat from the reaction zone, using active fillers, and changing the direction of adding the methyl chloride, we were able to increase the yield of dimethyldichlorosilane to 50%, increase its content in the condensate to 50-60%, and utilize the silicon to the extent of 70-80%.

## SUMMARY

1. A comparison of the activity of various types of contact masses revealed that in accordance with the proposed mechanism for the process, the most active contact mass is that in which the copper is most completely converted into intermetallic compound and the resulting compound has a highly developed active surface. A briquetted contact mass containing chemically precipitated copper and, as can be assumed on the basis of the obtained data, a silicon-copper alloy in the dustlike state, are such contact masses.

2. It was established that in association with a change in the composition of the contact mass during reaction there is a change in the composition of the reaction products. A study was made of the qualitative and quantitative composition of the reaction products and of its change during the course of reaction.

3. Due to the fact that the direct synthesis reaction is an exothermic process, running the synthesis under conditions that assure the removal of heat from the reaction zone, favors an increase in the yield of dimethyldichlorosilane. Chemically active metallic fillers, combining with the excess chlorine atoms, also show favorable influence in this respect.

## LITERATURE CITED

[1] A. L. Klebansky and V. S. Fikhtengolts, J. Gen. Chem. 26, 2502 (1956). *

[2] E. G. Rochow, J. Am. Chem. Soc. 67, 963 (1945).

[3] Yu. V. Karyakin, Pure Chemical Reagents (Goskhimizdat, 1947), 343. **

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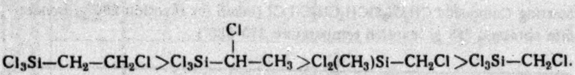
* Original Russian pagination. See C.B. Translation.

** In Russian.

# REACTION OF SOME γ-CHLOROALKYLSILANE CHLORIDES WITH SILICON UNDER THE CONDITIONS OF DIRECT SYNTHESIS

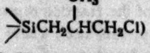
A. D. Petrov, S. I. Sadykh-Zade, V. A. Ponomarenko,
B. A. Sokolov, and Yu. P. Egorov

It was recently shown [1] that α- and β-chloroalkylsilane chlorides under the conditions of direct synthesis readily yield di- and trisilane chlorides in high yields. It was found that the reactivity of the α- and β-chloroalkylsilane chlorides decreases in the order



$$Cl_3Si{-}CH_2{-}CH_2Cl > Cl_3Si{-}\overset{Cl}{\overset{|}{C}}H{-}CH_3 > Cl_2(CH_3)Si{-}CH_2Cl > Cl_3Si{-}CH_2Cl.$$

The least reactive halide $Cl_3Si{-}CH_2Cl$ reacted to the extent of 65% and formed the di- and trisilane chlorides [types: $Cl_3SiCH_2SiCl_3$ and $(Cl_3SiCH_2)_2SiCl_2$] in 40% yield. The most reactive halide $Cl_3SiCH_2CH_2Cl$ under these conditions reacted completely and gave a mixture of di- and trisilane chlorides in 55% yield. It was also found that the main reaction – the direct synthesis reaction – is complicated to varying degree by side processes: 1) the formation of $HSiCl_3$, $SiCl_4$, $RSiHCl_2$, $RSiCl_3$ and 2) the reduction of the starting α- and β-chloroalkylsilane chlorides to the corresponding alkylsilane chlorides ($Cl_3SiCH_2CH_3$, $Cl_3SiCH_3$). Dehydrochlorination was also observed in the case of $Cl_3SiCH_2CH_2Cl$ and $Cl_3SiCHClCH_3$ with the formation, although in small amount, of vinyltrichlorosilane.

Continuing this investigation, we studied the behavior of the γ-chloroalkylsilane chlorides under the conditions of direct synthesis. As material for the study, the results of which are given in this communication, we used the γ-chloropropyl- and γ-chloroisobutylalkyldichlorosilanes, which were obtained by the addition of $(CH_3)Cl_2SiH$ and $(C_2H_5)Cl_2SiH$ to allyl chloride and methallyl chloride [2]. It was found that the indicated γ-silane chlorides react even more easily in the case of the direct synthesis reaction (reaction is quantitative even at 270°). However, here the main reaction is no longer the formation of di- and trisilane chlorides (the yield of which does not exceed 15-31%), but the dehydrochlorination reaction. Depending on the structure of the γ-chlorides the yield of dehydrochlorination products ranges from 58% (in the case of chlorides of type  $\rangle SiCH_2\overset{CH_3}{\overset{|}{C}}HCH_2Cl$) to 26% (in the case of chlorides of type $\rangle SiCH_2CH_2CH_2Cl$). When compared with the β-chloroalkylsilane chlorides, the higher yield of dehydrochlorination products obtained here, even for the γ-chloropropylsilane chloride, is evidently due to two factors: removal of the chlorine atom in the alkyl chain away from the silicon, and chiefly, replacement of one of the chlorine atoms in the trichlorosilyl group by an alkyl [3, 5]. The reaction for the dehydrochlorination of γ-chloroalkylsilane chlorides is reminiscent of the earlier studied [4] dehydrochlorination of 1,1-dichloroethane and 2,2-dichloropropane under the conditions of direct synthesis, with the difference that in the latter case the dehydrochlorination proceeded simultaneously with entrance into the direct synthesis reaction. It is interesting to mention that our studied dehydrochlorination of γ-chloroalkylchlorosilanes under the conditions of direct synthesis led to different results than those obtained when the same γ-chloroalkylchlorosilanes were subjected to dehydrochlorination in the presence of $AlCl_3$ [5].

Thus, for example, the dehydrochlorination of $(CH_3)Cl_2SiCH_2CH_2CH_2Cl$ with $AlCl_3$ gave only $CH_3SiCl_3$ (β-decomposition)* in almost quantitative yield. The dehydrochlorination of the same chloride under the conditions of direct synthesis led to the formation of $CH_3SiCl_3$ in a yield of only 14%; a mixture of allyl- and methylvinylmethyldichlorosilanes was formed in a yield of 24% (the remainder was decomposition and direct synthesis products, i. e., the corresponding di- and trisilane chlorides). The dehydrochlorination of γ-chloroisobutyltrichlorosilane with $AlCl_3$ led to the formation of a mixture of methallyl- and isocrotyl-trichlorosilanes in a 1 : 1 ratio. The dehydrochlorination of γ-chloroisobutylmethyldichlorosilane under the conditions of direct synthesis gave a mixture of butenylchlorosilanes in 42% yield, which mixture contained: γ-methylallyl-, isocrotyl- and methallylmethyldichlorosilanes in the ratio 50 : 40 : 10. As a result, in the last case we are dealing with more profound isomeric transformations, proceeding clear up to the formation of the skeletal isomer (γ-methylallyl-methyldichlorosilane).

## EXPERIMENTAL

The direct synthesis reaction with the above indicated γ-chlorides was run in a tube furnace at temperatures of 270-280, 370-380 and 470-480°. The γ-chlorides were passed through Pyrex glass tubes, having a diameter of 45 mm and a length of 600 mm, filled with a finely crushed silicon-copper alloy (80% Si, 20% Cu), at a rate of 25 g/hr. The reaction products were trapped in a water-cooled receiver, and then distilled through a column. Each narrow fraction was redistilled. The reaction conditions and the composition of the products obtained under these conditions are given in Tables 1-3. Since isomeric transformations [6] are possible in the dehydrochlorination of γ-chlorides, then to characterize them we took the Raman spectra of some of the dehydrochlorination products after their methylation (ethylation). Thus, for example, the wide boiling range of the fraction representing some of the dehydrochlorination products of $CH_3SiCl_2CH_2CH_2CH_2Cl$ (fraction with b. p. 116-122°, Table 1) permitted suspecting the presence of isomers. As the result of repeated distillation of this fraction we were able to divide it into two narrower fractions: 1st, b. p. 116-116.5° at 735 mm, $d_4^{20}$ 1.0758, $n_D^{20}$ 1.4390, and 2nd, b. p. 121-123° at 735 mm, $d_4^{20}$ 1.0742, $n_D^{20}$ 1.4370.

TABLE 1

Starting Compound $CH_3Cl_2SiCH_2CH_2CH_2Cl$ (taken for reaction 280 g; condensate obtained 255 g; reaction temperature 370-380°)

| Obtained | Amount (in g) | Boiling point | Amount in mixture (in %) |
|---|---|---|---|
| $CH_3Cl_2SiH$ . . . . . . . . . . . . | 2.8 | 40—42° | 1.1 |
| $SiCl_4$ . . . . . . . . . . . . . | 5.2 | 55—56 | 2.0 |
| $CH_3SiCl_3$ . . . . . . . . . . . . | 36.0 | 64—65.8 | 14.1 |
| $CH_3Cl_2SiCH_2CH{=}CH_2$<br>$CH_3Cl_2SiCH{=}CH{-}CH_3$ } . . . . | 60.0 | 16—122 | 23.5 |
| $CH_3Cl_2SiCH_2CH_2CH_2SiHCl_2$ . . . . | 18.2 | 206.5—207 | 7.1 |
| $CH_3Cl_2SiCH_2CH_2CH_2SiCl_3$ . . . . | 36.0 | 222.5—223 | 14.1 |
| $(CH_3Cl_2SiCH_2CH_2CH_2)_2$ . . . . . | 9.6 | 167—168.5 | 3.8 |
| $(CH_3Cl_2SiCH_2CH_2CH_2)_2SiCl_2$ . . . . | 9.0 | 166—168<br>(2 mm)<br>m.p. 29—30° | 3.5 |

The 1st fraction was ethylated by the use of ethylmagnesium bromide. The ethylation product after distillation through a column had the following constants: b. p. 142.5° at 770 mm, $d_4^{20}$ 0.7676, $n_D^{20}$ 1.4310. The Raman spectrum of this product was found to contain only the lines with the characteristic frequencies for $>\!Si{-}CH_2{-}CH{=}CH_2$ [7] (in $cm^{-1}$): 410, 890, 994, 1155, 1192, 1300, 1395, 1630, 2998, 3080, which clearly indicate that the ethylation product is methyldiethylallylsilane. The 2nd product after ethylation gave a product

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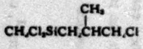
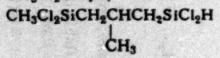
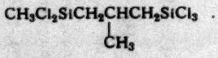
* However, the dehydrochlorination of $Cl_3SiCH_2CH_2CH_2Cl$ went with a 68% yield of a mixture.

TABLE 2

Starting Compound  $CH_3Cl_2SiCH_2\overset{CH_3}{\overset{|}{C}}HCH_2Cl$

| Obtained | Taken 300 g, condensate obtained 250 g, reaction temp. 270–280° | | | Taken 370 g, condensate obtained 320 g, reaction temp. 370–380° | | | Taken 300 g, condensate obtained 250 g, reaction temp. 470–480° | | |
|---|---|---|---|---|---|---|---|---|---|
| | boiling point | amount (in g) | % content in mixture | boiling point | amount (in g) | % content in mixture | boiling point | amount (in g) | % content in mixture |
| $HSiCl_3$ | 31–32° | 2.5 | 1.0 | 31.32° | 6.0 | 1.9 | 31–32° | 2.5 | 1.0 |
| $CH_3SiHCl_2$ | 41–42 | 19.0 | 7.6 | 41–42 | 7.0 | 2.2 | 41–42 | 6.0 | 2.4 |
| $SiCl_4$ | 56–57 | 14.0 | 5.6 | 56 | 10.0 | 3.1 | 55–56 | 13.0 | 5.2 |
| $CH_3SiCl_3$ | 65–66 | 15.0 | 6.0 | 65–66 | 50.4 | 15.8 | 65–66 | 11.0 | 4.4 |
| Mixture of dehydrochlorination products | | | | | | | | | |
| $CH_3Cl_2SiC_4H_7$ | 140–147 | 145.0 | 58.0 | 139–147 | 30.0 | 40.6 | 137–147 | 107.0 | 42.8 |
|  $CH_3Cl_2SiCH_2\underset{CH_3}{\underset{\vert}{C}}HCH_2SiCl_2H$ | 222–223 | 13.0 | 5.2 | 222–222.5 | 33.5 | 10.5 | 222–236 * | 15.0 | 6.0 |
|  $CH_3Cl_2SiCH_2\underset{CH_3}{\underset{\vert}{C}}HCH_2SiCl_3$ | 233–234 | 8.0 | 3.2 | 234–235 | 17.5 | 5.5 | — | — | — |
| Residue | — | 17.0 | — | — | 24.0 | — | — | 35.0 | — |

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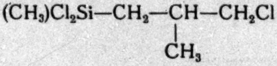
* Mixture of disilane chlorides.

TABLE 3

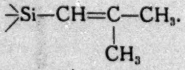
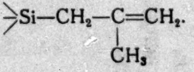
| Starting Compound $C_2H_5Cl_2SiCH_2CH_2CH_2Cl$ * | | | Starting Compound $C_2H_5Cl_2SiCH_2\overset{CH_3}{\overset{\vert}{C}}HCH_2Cl$ * | | |
|---|---|---|---|---|---|
| obtained | boiling point | amount (in %) | obtained | boiling point | amount (in %) |
| $C_2H_5SiCl_3$ | 97.5° | 5.8 | $HSiCl_3$ | 31—32° | 3.3 |
| $C_2H_5Cl_2SiCH_2CH=CH_2$<br>$C_2H_5Cl_2SiCH=CHCH_3$ | 144—149 | 25.9 | $SiCl_4$ | 56 | 1.2 |
| $C_2H_5Cl_2SiCH_2CH_2CH_2Si(Cl_2)H$ | 231 | 14.4 | $C_2H_5SiCl_3$ | 97.5 | 12.0 |
| $C_2H_5Cl_2SiCH_2CH_2CH_2SiCl_3$ | 241 | 17 | $C_2H_5Cl_2SiC_4H_7$ | 159—170 | 49.4 |
| Residue | — | 15 | $C_2H_5Cl_2SiCH_2\overset{CH_3}{\overset{\vert}{C}}HCH_2SiCl_2H$ | 235 | 9.1 |
| | | | $C_2H_5Cl_2SiCH_2\underset{CH_3}{\underset{\vert}{C}}HCH_2SiCl_3$ | 245—246 | 10 |
| | | | Residue | — | 6 |

* Reaction temperature 370-380°.

with the following properties: b. p. 142.5-143°, $d_4^{20}$ 0.7632, $n_D^{20}$ 1.4279. The Raman spectrum of this compound was observed to already contain two of the characteristic frequencies of the double bond: 1630 and 1620 $cm^{-1}$. The first frequency, and also the combination of the other frequencies, characteristic for $(C_2H_5)_2(CH_3)Si-CH_2-$ $-CH=CH_2$, proves the presence of the latter, the second frequency is characteristic for $\gt Si-CH=CH-CH_3$ [8]. In addition, other frequencies are observed in the spectrum: 390, 1039, 1315 and 1375 $cm^{-1}$, characteristic for propenylsilanes.

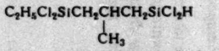
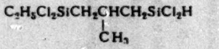
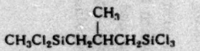
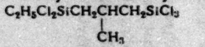
The fraction with b. p. 139-147° (Table 2), representing some of the dehydrochlorination products of  $(CH_3)Cl_2Si-CH_2-\underset{CH_3}{\underset{\vert}{C}}H-CH_2Cl$ was ethylated in exactly the same manner as before. The ethylation products after distillation through a column had the properties: b. p. 163-168° at 770 mm, $d_4^{20}$ 0.7795, $n_D^{20}$ 1.4378. The Raman spectrum of these products was observed to have the following frequencies (in $cm^{-1}$):

145(4sh), 163(2), 239(1b), 294(2b), 495(2), 574(5), 586(4), 660(1b), 749(0b), 801(0), 911(1b), 972(4), 1013(4), 1064(2), 1114(1b), 1163(5), 1233(3), 1259(1), 1306(4), 1326(1), 1378(4b), 1404(3b), 1415(4), 1444(4), 1462(6b), 1623(4sh), 1640(1), 1662(5sh), 2856(3), 2875(10), 2909(10), 2938(5), 2957(10), 2995(1), 3080(0).

The spectral region most characteristic for the double bond (1600 $cm^{-1}$) shows the presence of three compounds with the frequencies: 1623, 1640 and 1662 $cm^{-1}$. The 1623 $cm^{-1}$ frequency, as was mentioned earlier [8], together with the frequencies 1064, 1310 and 1370 $cm^{-1}$, is characteristic for the double bond in the isocrotyl group  $\gt Si-CH=\underset{CH_3}{\underset{\vert}{C}}-CH_3$. The very weak 1640 $cm^{-1}$ frequency could indicate the presence of the methallyl group  $\gt Si-CH_2-\underset{CH_3}{\underset{\vert}{C}}=CH_2$. The third very intense line with frequency 1662 $cm^{-1}$, corresponding to the main component of the mixture, could indicate the group $\gt Si-CH_2-CH=CH-CH_3$, which is also supported by the spectrum, available to us, of the earlier synthesized $(C_2H_5)_2(CH_3)Si-CH_2-CH=$ $=CH-CH_3$. The following frequencies were shown to be present (in $cm^{-1}$):

500(1b), 577(4b), 629(0), 702(0), 796(2), 814(2), 912(2), 972(2) 1013(2), 1042(1), 1114(3), 1165(4), 1242 (1 doublet), 1308(4), 1349(1), 1380(4), 1417(4), 1460(5), 1662(6sh).

TABLE 4

| Compound | Boiling point | $d_4^{20}$ | $n_D^{20}$ | $MR_D$ found | $MR_D$ calc. | Empirical formula | C found | C calc. | H found | H calc | Si found | Si calc. | Cl found | Cl calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3Cl_2SiCH_2CH_2CH_2SiCl_2H$<br>1-Methyldichlorosilyl-3-dichlorosilylpropane | 206.5—207 | 1.2450 | 1.4625 | 56.57 | 57.21 | $C_4H_{10}Cl_4Si_2$ | 23.09<br>22.84 | 22.2 | 4.59<br>4.43 | 4.44 | 20.69<br>20.76 | 20.74 | 50.46<br>51.69 | 52.59 |
| $C_2H_5Cl_2SiCH_2CH_2CH_2SiCl_2H$<br>1-Ethyldichlorosilyl-3-dichlorosilylpropane | 231—231.5 | 1.2386 | 1.4717 | 61.01 | 61.84 | $C_5H_{12}Cl_4Si_2$ | 22.12<br>22.23 | 22.23 | 4.46<br>4.32 | 4.48 | 20.80<br>20.83 | 20.78 | 52.70<br>52.16 | 52.51 |
| $C_2H_5Cl_2SiCH_2CH_2CH_2SiCl_3$<br>1-Ethyldichlorosilyl-3-trichlorosilylpropane | 241 | 1.2960 | 1.4728 | 66.27 | 65.84 | $C_5H_{11}Cl_5Si_2$ | 20.22<br>20.19 | 19.72 | 3.79<br>3.53 | 3.64 | 18.46<br>18.69 | 18.43 | 57.00<br>56.95 | 58.21 |
| <br>$C_2H_5Cl_2SiCH_2\underset{CH_3}{CH}CH_2SiCl_2H$<br>1-Methyldichlorosilyl-3-dichlorosilylisobutane | 222 | 1.2269 | 1.4707 | 61.47 | 61.84 | $C_5H_{12}Cl_4Si_2$ | 23.09<br>22.84 | 22.23 | 4.59<br>4.43 | 4.48 | 20.69<br>20.76 | 20.78 | 50.92<br>51.69 | 52.52 |
| <br>$C_2H_5Cl_2SiCH_2\underset{CH_3}{CH}CH_2SiCl_2H$<br>1-Ethyldichlorosilyl-3-dichlorosilylisobutane | 235.0 | 1.2100 | 1.4735 | 65.91 | 66.47 | $C_6H_{14}Cl_4Si_2$ | 25.90<br>25.98 | 25.36 | 4.85<br>4.90 | 4.97 | 19.28<br>19.06 | 19.75 | 49.60<br>49.90 | 49.92 |
| <br>$CH_3Cl_2SiCH_2\overset{CH_3}{CH}CH_2SiCl_3$<br>1-Methyldichlorosilyl-3-trichlorosilylisobutane* | 234—235 | — | — | — | — | $C_5H_{11}Cl_5Si_2$ | — | — | — | — | — | — | — | — |
| <br>$C_2H_5Cl_2SiCH_2\underset{CH_3}{CH}CH_2SiCl_3$<br>1-Ethyldichlorosilyl-3-trichlorosilylisobutane* | 245.0 | — | — | — | — | $C_6H_{13}Cl_5Si_2$ | — | — | — | — | — | — | — | — |
| $(CH_3Cl_2SiCH_2CH_2CH_2)_2$<br>1-Methyldichlorosilyl-6-methyldichlorosilylhexane | 167—188.5 | 1.2194 | 1.4938 | 74.46 | 74.22 | $C_8H_{18}Cl_4Si_2$ | 30.73<br>30.89 | 30.78 | 5.82<br>5.33 | 5.81 | — | — | 44.28<br>43.80 | 45.43 |
| $(CH_3Cl_2SiCH_2CH_2CH_2)_2SiCl_2$<br>1,1-bis-methyldichlorosilylpropyldichlorosilane | 166—168 | — | — | — | — | $C_8H_{18}Cl_6Si_3$ | — | — | — | — | — | — | — | — |

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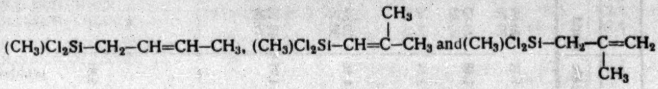
* For these compounds the elementary analysis data for some of the elements are somewhat above the permissible errors, but the products of either their methylation or ethylation show good analyses.

These frequencies were also observed in the spectrum of the ethylation products with b. p. 163-168° at 770 mm.

As a result, based on the ratio of the intensities of the above indicated characteristic frequencies for double bonds the dehydrochlorination product of $(CH_3)Cl_2Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Cl$ represented a mixture of three compounds:



$$(CH_3)Cl_2Si-CH_2-CH=CH-CH_3,\ (CH_3)Cl_2Si-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \text{ and } (CH_3)Cl_2Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

in the ratios 50 : 40 : 10. In addition, $(CH_3)ClSi-CH_2-CH=CH-CH_3$ was obtained by a different reaction, namely, by the addition of $CH_3Si(Cl_2)H$ to divinyl in an autoclave in the presence of platinum-on-carbon. The compound obtained after ethylation had the following properties: b. p. 161-162° at 736 mm, $d_4^{20}$ 0.7901, $n_D^{20}$ 1.4422, $MR_D$ 52.32; calc. 52.96. The spectrum of this compound was observed to contain the frequencies belonging to the radical $\geqslant Si-CH_2-CH=CH-CH_3$ (1662 $cm^{-1}$). The spectrum also contained the 1648 $cm^{-1}$ frequency, which probably corresponds to the cis-configuration of propylene. In addition to this, both the spectrum of the given compound and the spectrum of the same compound, but obtained by direct synthesis, contained the frequencies characteristic for the groups: $CH_3$ and $C_2H_5$ (700, 972, 1013, 1232, 1250, 1460 $cm^{-1}$) [9]. On the basis of this it is possible to conclude that in the given case, as is also evidently true in the case of $(C_2H_5)Cl_2Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Cl$, isomeric alkenylsilane chlorides are formed, not only with retention of the hydrocarbon skeleton $\geqslant Si-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$ and $\geqslant Si-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3$, , but also with its profound isomerization $\geqslant Si-CH_2-CH=CH-CH_3$, in which connection the last process is the principal one. The properties of the compounds that we were able to isolate from the mixtures in fairly pure form are listed in Table 4. The elementary analysis data for some of the compounds exceeded somewhat the permissible errors, but even in these cases after ethylation the analysis data usually agreed with calculation. For these compounds (they are designated by an asterisk) only the boiling points are given in the table.

## SUMMARY

1. It was shown that the γ-chloroalkylalkyldichlorosilanes react more readily with silicon under the conditions of direct synthesis than do the α- and β-chloroalkylsilane chlorides. Here, in contrast to the α- and β-chlorides, the main reaction is not the formation of di- and trisilane chlorides, but the dehydrochlorination of the starting γ-chlorides to the corresponding unsaturated compounds.

2. It was found that the dehydrochlorination of γ-chlorides under the conditions of direct synthesis is accompanied by isomeric transformations, which leads to the formation, in the case of the γ-chloropropylalkyldichlorosilanes, of the corresponding allyl- and propenylsilane chlorides, and in the case of the γ-chloroisobutylalkyldichlorosilanes, mainly of the isocrotylalkyldichlorosilane, and as the result of skeletal isomerization of the hydrocarbon chain, of the γ-methylallylalkyldichlorosilane.

## LITERATURE CITED

[1] S. I. Sadykh-Zade, E. A. Chernyshev, and V. F. Mironov, Proc. Acad. Sci. USSR 105, 496 (1955); A. D. Petrov, S. I. Sadykh-Zade, E. A. Chernyshev, and V. F. Mironov, J. Gen. Chem. 26, 1248 (1956).*

[2] V. A. Ponomarenko, B. A. Sokolov, Kh. M. Minachev, and A. D. Petrov, Proc. Acad. Sci. USSR 106, 76 (1956).*

[3] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and Yu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, 310.*

[4] A. D. Petrov, S. I. Sadykh-Zade, and I. I. Tsetlin, Proc. Acad. Sci. USSR 107, 99 (1956).*

[5] A. D. Petrov, V. F. Mironov, and I. D. Mashantsker, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 550.*

[6] D. L. Bailey and A. N. Pines, Ind. Eng. Chem. 46, 2363 (1954).

[7] Yu. P. Egorov and P. A. Bazhulin, Proc. Acad. Sci. USSR 88, 47 (1953).

[8] A. D. Petrov, Yu. P. Egorov, V. F. Mironov, G. I. Nikishin, and A. A. Bugorkova, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 50.*

[9] A. F. Plate, N. A. Momma, and Yu. P. Egorov, Proc. Acad. Sci. USSR 97, 847 (1954).

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* Original Russian pagination. See C.B. Translation.

## SYNTHESIS AND TRANSFORMATIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

### VI. REACTION OF HYDROGEN-CONTAINING ALKYL(ARYL)DICHLOROSILANES WITH ORGANIC ALCOHOLS

M. F. Shostakovsky, D. A. Kochkin, V. L. Vinogradov, and V. A. Neterman

The reaction of hydrogen-containing alkyl(aryl)halosilanes with alcohols and their alcoholates has not been investigated. There exists only a brief communication by the authors of the present paper [1]. As was established by us, depending on the amount of alcohol taken for reaction, the reaction of alkyldihalosilanes with alcohols yields alkylhaloalkoxy-, alkyldialkoxy- and trialkoxysilanes. It is possible to assume that the arylhalosilanes will also react with alcohols, in accordance with the following equations:

1. $RSiHX_2 + R'OH \xrightarrow{\text{or}\quad R'OMe} RSiH(OR')X + HX(MeX)$
2. $RSiHX_2 + 2R'OH \longrightarrow RSiH(OR')_2 + 2HX$
3. $RSiHX_2 + 3R'OH \longrightarrow RSi(OR')_3 + 2HX + H_2$
4. $RSiHX_2 + R'OH \longrightarrow RSiH(OR')X + HX$
5. $RSiH(OR')X + R'OH \longrightarrow RSiH(OR')_2 + HX$
6. $RSiH(OR')_2 + R'OH \longrightarrow RSi(OR')_3 + H_2$ or
7. $RSiHX_2 \xrightarrow{R'OH} RSiH(OR')X \xrightarrow{R'OH} RSiH(OR')_2 \xrightarrow{R'OH} RSi(OR')_3$,

where $R = CH_3, C_2H_5,$ & $R' = C_2H_5, C_4H_9$ etc.

In this paper we describe the reaction of methyl- and ethyldichlorosilanes with ethyl and butyl alcohols. The names and formulas of the compounds isolated from the reaction products are given in the table. Of them, compounds (I-IV) and (IX, X) are new. As had been established by us, the reaction of methyl- and ethyldichlorosilanes with alcohols, taken in a 1 : 1 ratio (Eq. 1), yields mainly haloalkylalkoxysilanes, and when taken in a 1 : 2 ratio (Eq. 2), mainly hydrogen-containing alkyldialkoxysilanes. With an excess of the alcohol the hydrogen atom is also etherified with the formation of mainly trialkoxysilanes (Eq. 3). The formation of these compounds can also be depicted by Eqs. (4-7), which show the stepwise and consecutive formation of a series of intermediate compounds. The latter were isolated by us both from the reaction products of the chloride with excess alcohol (Eq. 3) and when the latter was present in deficient amount (Eqs. 1 and 2).

The high reactivity shown by alkylhalosilanes with hydrogen atoms was established from the performed investigations. Earlier we had established that the hydrogen atom is easily hydrolyzed in alkaline medium. Thus, for example, the hydrolysis of methyl- and ethyldichlorosilanes yielded solid high-molecular compounds [2]. The high reactivity shown by the hydrogen-containing compounds in the formation of vinyl compounds of silicon was also established in their reaction with acetylene, named by us as the vinylation reaction [3]. The reaction described below for the alcoholysis or etherification of alkyl(aryl)halosilanes represents definite interest, since it permits obtaining alkoxy (or aroxy)silanes from the halides of hydrogen-containing silicon derivatives. The described reactions of hydrolysis, vinylation and etherification establish the exceptional reaction properties of such compounds and, in particular, of their hydrogen atom. The hydrogen-containing alkylhaloalkoxy-, alkyldialkoxy- and trialkoxysilanes represent mobile liquids with an ethereal odor, soluble in ether, alcohol, acetone and other solvents, and insoluble in water. When distilled at atmospheric pressure they decompose with the formation of

| Expt. Nos. | Name of compound | Formula | Boiling point and pressure (in mm) | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|---|
| (I) | Methyldiethoxysilane | $CH_3SiH(OC_2H_5)_2$ | 42° (110) | 1.3800 | — |
| (II) | Methyldibutoxysilane | $CH_3SiH(OC_4H_9\text{-n})_2$ | 80 (8.5) | 1.4040 | 0.8454 |
| (III) | Ethyldiethoxysilane | $C_2H_5SiH(OC_2H_5)_2$ | 24—25 (15) | 1.3850 | 0.8466 |
| (IV) | Ethyldibutoxysilane | $C_2H_5SiH(OC_4H_9\text{-n})_2$ | 89—90.6 (19) | 1.4085 | 0.8465 |
| (V) | Methyltriethoxysilane• | $CH_3Si(OC_2H_5)_3$ | 142—144.5 (742), 66 (64), 57 (37) | 1.3820 | 0.8911 |
| (VI) | Methyltributoxysilane• | $CH_3Si(OC_4H_9\text{-n})_3$ | 114.5 (7), 115 (8) | 1.4118 | 0.8776 |
| (VII) | Ethyltriethoxysilane• | $C_2H_5Si(OC_2H_5)_3$ | 69 (22), 157 (747) | 1.3900 | 0.8954 |
| (VIII) | Ethyltributoxysilane• | $C_2H_5Si(OC_4H_9\text{-n})_3$ | 134 (16), 135 (17) | 1.4140 | 0.8783 |
| (IX) | Methylethoxychlorosilane•• | $CH_3SiH(Cl)(OC_2H_5)$ | 68 (755.5) | 1.3878 | 0.9374 |
| (X) | Ethylbutoxychlorosilane••• | $C_2H_5SiH(Cl)(OC_4H_9\text{-n})$ | 60 (34.5) | 1.4126 | 0.9285 |

|  | $MR_D$ |  | Empirical formula | C (%) |  | H (%) |  | Si (%) |  | Yield, based on chloride (in %) |
|---|---|---|---|---|---|---|---|---|---|---|
|  | found | calc. |  | found | calc. | found | calc. | found | calc. |  |
| (I) | — | 36.69 | $C_5H_{14}O_2Si$ | 44.75, 44.85 | 44.76 | 10.12, 10.15 | 10.49 | 20.87, 20.89 | 20.94 | 32 |
| (II) | 55.03 | 55.21 | $C_9H_{22}O_2Si$ | 56.79, 56.80 | 56.84 | 11.46, 11.50 | 11.56 | 14.70, 14.69 | 14.77 | 68 |
| (III) | 41.03 | 41.32 | $C_6H_{16}O_2Si$ | 48.38, 48.41 | 48.65 | 10.81, 11.00 | 10.81 | 18.60, 18.64 | 18.92 | 46 |
| (IV) | 59.58 | 59:84 | $C_{10}H_{24}O_2Si$ | 59.04, 59.11 | 58.81 | 12.08, 12.01 | 11.76 | 13.37, 13.43 | 13.75 | 35 |
| (V) | 46.54 | 46.45 | $C_7H_{18}O_3Si$ | 47.17, 47.22 | 47.18 | 10.23, 10.22 | 10.12 | 15.98, 16.04 | 15.73 | 48 |
| (VI) | 74.39 | 74.23 | $C_{13}H_{30}O_3Si$ | 59.74, 59.52 | 59.47 | 11.73, 11.69 | 11.43 | 10.71, 10.46 | 10.74 | 45 |
| (VII) | 50.93 | 51.08 | $C_8H_{20}O_3Si$ | 50.25, 50.10 | 50.00 | 10.16, 10.27 | 10.42 | 14.40, 14.69 | 14.58 | 52 |
| (VIII) | 78.67 | 78.86 | $C_{14}H_{32}O_3Si$ | 60.78, 60.55 | 60.80 | 11.71, 11.63 | 11.57 | 10.40, 10.70 | 10.16 | 65 |
| (IX) | 30.83 | 30.93 | $C_3H_9OClSi$ | 29.23, 29.00 | 28.92 | 7.10, 7.18 | 7.22 | 22.40, 22.34 | 22.54 | 65 |
| (X) | 44.71 | 44.82 | $C_6H_{15}OClSi$ | 43.15, 43.20 | 43.26 | 8.93, 8.97 | 9.00 | 16.75, 16.80 | 16.86 | 85 |

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• According to the literature data, (V) has b. p. 143°, $n_D^{20}$ 1.3835, $d_4^{20}$ 0.8923 [4]; (VI) b. p. 115° at 10 mm, $n_D^{20}$ 1.4106, $d_4^{20}$ 0.8775 [5]; (VII) – b. p. 158.5°, $d_0^{0}$ 0.9207 [6]; b. p. 158-160°, d 0.9281, $n_D$ 1.3853 [7]; (VIII) – b. p. 237°, $n_D$ 1.4128 [4].

•• Found %: Cl 28.30, 28.40. $C_3H_9OClSi$. Calculated %: Cl 28.47.

••• Found %: Cl 21.00, 20.91. $C_6H_{15}OClSi$. Calculated %: Cl 21.28.

highly-condensed compounds. The alkylhaloalkoxysilanes represent more stable compounds, and some of them can be distilled at atmospheric pressure without decomposition; however, they are easily hydrolyzed and fume in the air.

## EXPERIMENTAL

1. Preparation of methylchloroethoxysilane (IX) (chloride : alcohol ratio = 1 : 1). Into a three-necked flask, cooled with a mixture of ice and salt, and fitted with a dropping funnel and reflux condenser with calcium chloride tube, was charged 115.02 g (1 g-mole) of methyldichlorosilane (b. p. 41.0-42.0°, $d_4^{20}$ 1.1047), and then 46.0 g of ethyl alcohol• was added in drops. Here the temperature of the reaction mixture dropped at first to 3-4° due to solution of the methyldichlorosilane and hydrogen chloride in the alcohol; the reaction did not begin until the reaction mixture was completely saturated with hydrogen chloride. Then a stormy exothermic reaction set in with much evolution of hydrogen chloride. In cooling the flask with reaction products in an ice-salt mixture care must be taken to keep the temperature below +10°. The reaction mixture was heated at the boil for 20-30

min until the evolution of hydrogen chloride had ceased; here the boiling point of the reaction products rose to 80-90°. The mixture was let stand overnight, after which it was fractionated through a rectification column in a stream of dry nitrogen. Here we isolated: 85.8 g (70.1%) of methylchloroethoxysilane (IX), 5.6 g of a fraction with b. p. 34-38° (100 mm), $n_D^{20}$ 1.3851, $d_4^{20}$ 0.9188, from which after a second fractionation in vacuo, in a stream of nitrogen, from a Favorsky flask, we isolated methyldiethoxysilane (I), and 10.9 g of high-boiling tarry products.

2. Preparation of methyldiethoxysilane (I) (chloride : alcohol ratio = 1 : 2). Into a flask was charged 115.02 g (1 g-mole) of methyldichlorosilane and then 92.0 g (2 g-moles) of dehydrated ethyl alcohol was added. The reaction products were heated to 110° for 1.0-1.5 hrs (until the evolution of hydrogen chloride ceased). Vacuum-fractionation in a stream of dry nitrogen through a rectification column gave 4.1 g of methylchloroethoxysilane (IX), 53.9 g (40%) of methyldiethoxysilane (I) and 13.4 g of high-boiling products.

3. Preparation of methyltriethoxysilane (V) (chloride : alcohol ratio = 1 : 3). To 138.0 g of ethyl alcohol (3 g-moles) was added 115.02 g of methyldichlorosilane in drops from a separatory funnel; here the temperature of the reaction mixture did not rise above 10-15°. After adding the chloride the mixture was refluxed on the water bath for 5-6 hrs; here the boiling point of the reaction mixture gradually rose to 110°. The evolution of hydrogen chloride was complete after such prolonged heating. Vacuum-fractionation of the reaction products in a stream of nitrogen gave 6.9 g of methyldiethoxysilane (I), 115.8 g (65%) of methyltriethoxysilane (V) and 32.5 g of high-boiling compounds. When the reaction products were fractionally distilled at atmospheric pressure the yield of methyltriethoxysilane was sharply reduced, and it dropped to 20-25%; at the same time the yield of high-boiling compounds showed a sharp increase. This observation is valid for all of the syntheses described below.

4. Preparation of ethylchlorobutoxysilane (X) (chloride : alcohol ratio = 1 : 1). Into a flask, cooled with ice and salt, was charged 129.0 g (1 g-mole) of ethyldichlorosilane [b. p. 74-76° (746 mm), $n_D^{20}$ 1.4216], and then 79.04 g (1 g-mole) of butyl alcohol (anhydrous) was added in drops. The temperature of the reaction medium did not rise above +20°. The reaction mixture was heated at the boil for 30-40 min at 120° and then allowed to stand overnight, after which it was vacuum-fractionated through a rectification column (20 theoretical plates) in a stream of dry nitrogen. Here we isolated 116.8 g (85.0%) of ethylbutoxychlorosilane (X), 17.5 g of a fraction with b. p. 67.0° (26.0 mm), 68.0° (29.0 mm), $n_D^{20}$ 1.4115, $d_4^{20}$ 0.8670, from which ethyldibutoxysilane (IV) was isolated after a second fractionation in vacuo, and 18.0 g of high-boiling products. Ethylchlorobutoxysilane (X) is a colorless, fuming liquid with a sharp ethereal odor, explodes when heated, dissolves in the common solvents, and is easily hydrolyzed. It distills in vacuum, in a stream of nitrogen, without decomposition.

5. Preparation of ethyldibutoxysilane (IV) (chloride : alcohol ratio = 1 : 2). Into a flask was charged 129 g (1 g-mole) of ethyldichlorosilane and then 148.08 g (2 g-moles) of anhydrous butyl alcohol was added in drops. After adding the alcohol the reaction mixture was heated at 120-130° for 1.5-2.0 hrs and then allowed to stand overnight. Fractionation of the reaction products through a column gave 71.4 g (35.0%) of ethyldibutoxysilane (IV), 40.8 g (14.4%) of ethyltributoxysilane (VIII) and 49.4 g of high-boiling residues. In the trap, cooled in a mixture of dry ice and acetone, 3.4 g of a liquid with a sharp odor was collected, which was mainly ethylchlorobutoxysilane (X).

6. Preparation of ethyltributoxysilane (VIII) (chloride : alcohol ratio = 1 : 3). To 129 g of ethyldichlorosilane was added 225 g (3 g-moles) of butyl alcohol in drops. The reaction products were heated at the boil under reflux for 10-12 hrs; here the temperature gradually rose to 180°. Fractionation of the mixture gave 30.0 g (14.7% based on the chloride) of ethyldibutoxysilane (IV), 176.4 g (65.0%) of ethyltributoxysilane (VIII) and 84.0 g of high-boiling products.

7. Reaction of ethyldichlorosilane with the alcoholate of butyl alcohol. Into a flask, cooled in ice, was charged 300 g of butyl alcohol, and then 13.0 g of metallic sodium was added in small pieces. Then to the alcoholate solution was added 129 g (1 g-mole) of ethyldichlorosilane with cooling. Strong exothermic reaction was observed here and the deposition of a white flocculent precipitate. The reaction products were heated

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* All of the alcohols were dehydrated by refluxing over calcium oxide and then distilling twice from a flask with dephlegmator.

at the boil for 12 hrs. The final boiling temperature of the reaction mixture was 160°. After filtration and fractionation we obtained 16.0 g(7.8%, based on the chloride) of ethyldibutoxysilane (IV), 229.0 g (83.0%) of ethyltributoxysilane (VIII) and 18.0 g of tarry high-boiling compounds.

The properties of the other compounds synthesized by us are given in the table. They were obtained in a similar manner.

## SUMMARY

1. The reaction of hydrogen-containing alkyldichlorosilanes with organic alcohols was investigated.

2. It was established that when the alkylhalosilane : alcohol ratio is equal to 1 : 1 the main reaction products are the alkylhaloalkoxysilanes $RSiH(OR')X$, when the ratio is equal to 1 : 2 the main reaction products are the alkyldialkoxysilanes $RSiH(OR')_2$, and when the ratio is equal to 1 : 3 or an excess of alcohol is used the main products are the alkyltrialkoxysilanes $RSi(OR')_3$.

3. The previously unknown methylethoxychlorosilane (IX), ethylbutoxychlorosilane (X), methyl- and ethyldiethoxysilanes (I) and (III), methyldibutoxysilane (II) and ethyldibutoxysilane (IV) were isolated and characterized, and we also characterized the methyl- and ethyltriethoxysilanes (V) and (VII), and the methyl- and ethyltributoxysilanes (VI) and (VIII).

## LITERATURE CITED

[1] M. F. Shostakovsky, D. A. Kochkin, V. L. Vinogradov, and V. A. Neterman, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1956, 1269.*

[2] M. F. Shostakovsky, D. A. Kochkin, Kh. I. Kondratyev, and V. M. Rogov, J. Gen. Chem. 26, 3344 (1956).*

[3] M. F. Shostakovsky and D. A. Kochkin, Proc. Acad. Sci. USSR 109, 113 (1956);* M. F. Shostakovsky, K. A. Andrianov, D. A. Kochkin and V. L. Vinogradov, Author's Certificate No. 105407 (1956).

[4] H. W. Post and Ch. H. Hofrichter, J. Org. Chem. 5, 443 (1940).

[5] R. O. Sauer, J. Am. Chem. Soc. 68, 138 (1946).

[6] A. Ladenburg, Ber. 4, 726 (1871).

[7] K. A. Andrianov and O. I. Gribanova, J. Gen. Chem. 8, 558 (1938).

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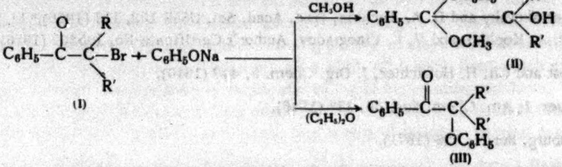
* Original Russian pagination. See C.B. Translation.

# CHEMICAL TRANSFORMATIONS OF α-HALO KETONES*

## V. ACTION OF SODIUM ARYLATES ON α-BROMO KETONES OF ALKAROMATIC SERIES

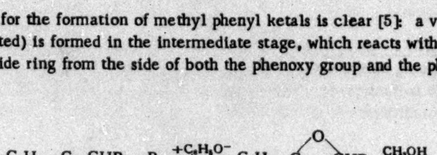
T. I. Temnikova, G. A. Ugolnikova, O. A. Netsetskaya, and T. B. Remizova

It was first shown on the example of α-bromoethyl phenyl ketone that in the reaction of sodium phenolate with α-halo ketones of the alkaromatic series the process, depending on the nature of the solvent, can go in two different directions: in methyl alcohol solution – in the direction of forming the methyl phenyl ketals of the keto alcohols, corresponding to the bromo ketone, and when absolute ether is used as the solvent – in the direction of the phenoxy ketone; the same reaction course as the latter is also observed in acetone solution. Later [3] it was shown that other bromo ketones of the alkaromatic series, independent of the length and branching of the alkyl chain, yield methyl phenyl ketals when the reaction is run in methyl alcohol.



As had already been mentioned earlier [4], apparently in all cases the first reaction to take place in the action of nucleophilic reagents on α-halo ketones is reaction between the reagent and the carbon atom of the carbonyl group of the halo ketone; the structure of the final reaction product depends on the nucleophilic properties of the reagent, the reaction conditions used, and the structure of the halo ketone.

The mechanism for the formation of methyl phenyl ketals is clear [5]: a very reactive α-phenoxy oxide (which cannot be isolated) is formed in the intermediate stage, which reacts with the solvent – methyl alcohol – with opening of the oxide ring from the side of both the phenoxy group and the phenyl group, in accordance with the scheme



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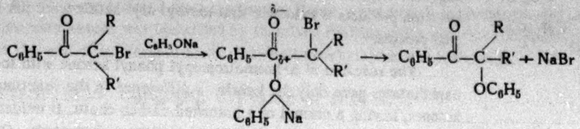
* The present paper is a direct continuation of a number of papers, published under the general title "Anomalous Reactions of Bromo Ketones" [1].

It is possible that the formation of phenoxy ketones occurs in those cases where in the reaction of the sodium phenolate with the carbon atom of the carbonyl group the formation of a valence bond between the oxygen and the carbon fails to be achieved, and the phenoxy group migrates to the adjacent atom. It is possible to depict the process as proceeding by the scheme



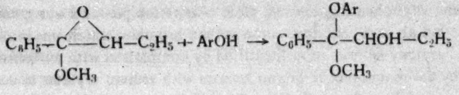
A difference in the direction of the process in different types of solvents can be explained by saying that in alcohols the effective agent is the phenolate ion, while in ether it is the sodium phenolate (the sodium phenolate with acetone gives a complex compound).

It seemed of interest to verify the validity of the expressed considerations relative to the mechanism of formation of phenoxy ketones by resort to the method of varying the degree of nucleophilicity of the phenyl component of the reaction, running the process with phenols substituted in the ring with groups of different electrochemical character. It could be expected that using the more acidic phenols, being less nucleophilic, will result in a decreased tendency to form mixed ketals and will increase the probability of the reaction going in methyl alcohol solutions in the direction of the phenoxy ketones.

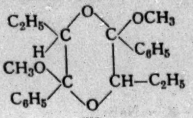
Yields of Products from the Reaction of α-Bromopropyl Phenyl Ketone with Sodium Arylates in $CH_3OH$ Solution as a Function of the $pK_a$ of the Corresponding Phenol

| | $pK_a$ | Yield of reaction products (in %) | |
|---|---|---|---|
| | | ketal | phenoxy ketone |
| Phenol . . . . . . . | 9.95 | 60 | 20 |
| β-Naphthol . . . . | 9.91 | 15 | 40 |
| α-Naphthol . . . . | 9.83 | – | 50 |
| p-Chlorophenol. . | 9.38 | – | 66 |

In the present paper we studied the reaction in methyl alcohol solution of α-bromopropyl phenyl ketone and α-bromoisopropyl phenyl ketone with the sodium α- and β-naphtholates, p-nitrophenolate and 3,4-xylenolate, and also the reaction between sodium p-chlorophenolate and α-bromopropyl phenyl ketone. The results of the study are summarized in the table, where the $pK_a$ of the corresponding phenols are also given. From the data in the table it can be seen that a change from sodium phenolate to the only slightly less nucleophilic sodium β-naphtholate leads to the formation, together with the methyl naphthyl ketal, of a substantial amount of the naphthoxy ketone. Under the influence of even less nucleophilic reagents – the α-naphtholate and the p-chlorophenolate – only the corresponding aryloxy ketones are formed, in which connection the yield of the latter is increased. To derive some valid conclusions relative to the reaction course we prepared, starting from the methyllactolide of ethylbenzoylcarbinol, the corresponding ketals.



The ketals obtained in the reaction with p-chlorophenol and p-nitrophenol proved to be unstable and when heated in methyl alcohol solutions they gradually decomposed with the formation of the corresponding phenols and the cyclodimethyldilactolide of ethylbenzoylcarbinol (IV). Since the aryloxy ketones were recrystallized from alcohol it is possible that the ketals formed together with them could have been decomposed here. However, the absence of a high-melting, easily crystallized and readily identified product (IV) among the reaction products is evidence that methyl aryl ketals were not formed in the reaction process.


(IV)

The reaction of α-bromoisopropyl phenyl ketone with sodium α- and β-naphtholates gave only the ketals; a difference in the reaction course with bromo ketones, having a normal or a branched carbon chain, is evidently due to the steric hindrance encountered in the approach of bulky naphthyl nuclei to a tertiary carbon atom. Only the α-nitrophenoxy ketone was obtained when α-bromoisopropyl phenyl ketone was reacted with the even less nucleophilic sodium p-nitrophenolate. The reaction of the bromoisopropyl phenyl ketone with the more nucleophilic sodium 3,4-xylenolate gave only the ketal.

Together with studying the reaction course when operating in methyl alcohol solutions, we ran some experiments on the preparation of the corresponding aryloxy ketones under the usual conditions (in acetone solutions), and also of methyl aryl ketals, starting with the methyllactolides of α-keto alcohols. In the preparation of α-naphthoxypropyl phenyl ketone and the methyl α-naphthyl ketal of ethylbenzoylcarbinol we observed the formation of two modifications – a low-melting and a high-melting. In both cases the low-melting modification is easily converted into the high-melting by fusion of the mixture; in the first case the same transition was also observed when the mixture was heated with an aqueous alcohol solution of either an acid or alkali.

In addition to the above described reactions, we studied the reaction of α-bromoethyl phenyl ketone with sodium p-nitrophenolate in methyl alcohol solutions, and also of α-bromobutyl phenyl ketone with sodium phenolate and the cresylate; the same as in the other cases, the reaction with the p-nitrophenolate gave the nitrophenoxy ketone, while the reaction with sodium phenolate or with the somewhat more basic sodium cresylate gave only the methyl aryl ketals.

All of the aryloxy ketones are stable and do not change when heated with aqueous alcohol solutions of either acids or alkalies. All of the methyl aryl ketals of the α-keto alcohols are easily hydrolyzed when heated with dilute aqueous alcohol solutions of sulfuric acid to yield the corresponding α-keto alcohols and phenols. Mixed ketals with a low stability were obtained from the more acidic phenols, especially from the nitrophenol (see above). The mixed ketals, containing either the naphthyl or the xylenyl radical, corresponding to the dimethylbenzoylcarbinol, are easily hydrolyzed when kept in the open. Gradual decomposition of the substance is observed and the easily formed anhydro dimer of the dimethylbenzoylcarbinol with m. p. 185-186° is obtained, first described by A. E. Favorsky and N. Mandryka [7]. It is possible that such easy decomposition was due to the presence of acidic vapors in the laboratory, and also due to the fact that the dimerization of the dimethylbenzoylcarbinol is accompanied by the cleavage of water.

## EXPERIMENTAL

Reaction of sodium arylates with α-bromo ketones in methyl alcohol. The reaction was run in the following manner: to a solution of sodium arylate, prepared by the addition of the calculated amount of the phenol to a solution of sodium methylate in methyl alcohol, was added an equimolar amount of the bromo ketone, dissolved in an equal volume of methyl alcohol. In most of the experiments the reaction mixture was heated at 40-50° with constant stirring until the test for organic halogen was negative. Usually the visible formation of sodium bromide began within an hour, and the reaction was complete in 5-6 hrs. The formed sodium bromide was filtered and the methyl alcohol was removed in vacuo without heating (usually strong tarring occurred if the methyl alcohol was distilled off even with slight heating, and the yield of reaction products was greatly reduced). The residue after removal of the methyl alcohol contained some sodium bromide, which was removed by washing with water. The obtained ketals and aryloxy ketones were identified by comparison with authentic specimens. The α-aryloxy ketones were obtained by the reaction of α-bromo ketones with sodium arylates in acetone solution [2]. The methyl aryl ketals were prepared from the methyllactolides of the corresponding α-keto alcohols and phenols in benzene solution in the cold [1, 3].

## I. Reaction of α-Bromopropyl Phenyl Ketone* with Sodium Arylates

a) Reaction with sodium phenolate.** The reaction was run with 15 g of the bromo ketone. Removal of the methanol left a crystalline mixture of sodium bromide and organic compound. The sodium bromide was removed by washing with water; the crystals, after drying, were recrystallized from methyl alcohol and had m. p. 143.5°, which corresponds to the methyl phenyl ketal of ethylbenzoylcarbinol [3]; the yield was 60%. Crystals with m. p. 69-70° were isolated from the mother liquor, representing α-phenoxypropyl phenyl ketone (~ 20%). The α-phenoxy ketone was identified by its mixed melting point with the compound prepared by Bradsher and Rosher [2], and characterized as the 2,4-dinitrophenylhydrazone with m. p. 59-60°.

Found %: N 13.25, 13.27. $C_{22}H_{20}O_5N_4$. Calculated %: N 13.34.

α-Phenoxypropyl phenyl ketone does not change when heated with $ZnCl_2$ in ether, or when heated with methyl alcohol in the presence of either conc. $H_2SO_4$ or HCl.

b) Reaction with sodium β-naphtholate.*** The reaction was run using 10 g of bromo ketone and 1.01 g of Na and 6.4 g of β-naphthol. The substance was recrystallized from aqueous methyl alcohol. We obtained 5.2 g of colorless needle crystals with m. p. 83-84°.

Found %: C 82.96, 82.77; H 6.46, 6.25. $C_{20}H_{18}O_2$. Calculated %: C 82.76; H 6.20.

The 2,4-dinitrophenylhydrazone of the ketone has m. p. 177-179°.

Found %: N 12.17, 12.14. $C_{26}H_{22}N_4O_5$. Calculated %: N 12.34.

β-Naphthoxypropyl phenyl ketone does not change when heated with a 5% aqueous alcohol solution of potassium hydroxide (the solution acquires a cherry-red color), or when heated with a 5% aqueous alcohol solution of sulfuric acid.

Found %: 78.20, 78.24; H 7.05, 7.09; $OCH_3$ 9.60, 9.51; act. H 1.11, 1.10. $C_{21}H_{22}O_3$. Calculated %: C 78.26; H 6.83; $OCH_3$ 9.63; act. H 1.

The white hard granules that deposited from the mother liquor were recrystallized from petroleum ether. We obtained 0.92 g of the methyl β-naphthyl ketal of ethylbenzoylcarbinol with m. p. 111-112°.

For its identification the methyl β-naphthyl ketal of ethylbenzoylcarbinol was prepared in the following manner. A solution of 2 g of the naphthol in benzene was treated with 2.5 g of the methyllactolide of ethylbenzoylcarbinol; the evolution of heat was not observed. The next day the benzene was removed in vacuo without heating. The yield of crude product was nearly quantitative. The precipitate was recrystallized several times from petroleum ether, m. p. 111°; the mixed melting with the ketal, prepared from the bromo ketone, was not depressed.

c) Reaction with sodium α-naphtholate.**** The reaction was run using 1.01 g of sodium, 6.4 g of the naphthol, 6.25 ml of methyl alcohol and 10 g of the bromo ketone. Strong tarring occurred when the mixture was heated, so the experiment was run in the cold with vigorous stirring. The reaction was complete in several hours. Approximately $^1/_3$ of the methyl alcohol was removed by vacuum-distillation, the NaBr was filtered, and the filtrate was poured into a crystallizing dish. The whole mass crystallized in an hour. The slightly greenish crystals were washed with methyl alcohol and then recrystallized from it twice. α-Naphthoxypropyl phenyl ketone with m. p. 75-76° was obtained in 50% yield. We failed to isolate any other crystalline products.

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* α-Bromopropyl phenyl ketone had the following constants: b. p. 132° at 8 mm, and 124° at 5 mm.

** Done by G. A. Ugolnikova.

*** Done by O. A. Netsetskaya.

**** Done by O. A. Netsetskaya.

Found %: C 82.60, 82.49; H 6.41, 6.29. $C_{20}H_{18}O_2$. Calculated %: C 82.76; H 6.20.

When the α-naphthoxypropyl phenyl ketone was heated with a 5% aqueous alcohol solution of KOH for 1 hr the solution acquired a raspberry color. A small amount of colorless crystals, melting at 75°, deposited on cooling. The addition of water to the raspberry-colored solution gave a colorless precipitate; it was recrystallized from methyl alcohol, but the obtained crystals melted much higher than the original – at 86-87°.

Found %: C 82.42; H 6.42. $C_{20}H_{18}O_2$. Calculated %: C 82.76; H 6.20.

A similar change in the melting point of α-naphthoxypropyl phenyl ketone was also observed when it was heated in an aqueous alcohol solution of sulfuric acid (an alcohol solution of the ketone was treated with 5% aqueous $H_2SO_4$ solution until cloudiness appeared). The solution was heated for 1 hr at the boil. Colorless crystals with m. p. 86° deposited when the solution was cooled. Addition of water to the mother liquor gave a precipitate, which was recrystallized from methyl alcohol. M. p. 86-87°. The yield was quantitative.

Found %: C 82.68; H 6.41. $C_{20}H_{18}O_2$. Calculated %: C 82.76; H 6.20.

Mixtures of all proportions of starting ketone with m. p. 75-76° and the crystals, obtained in the treatment with either alkali or acid and having m. p. 86-87°, melted sharply at 86-87°.

*d) Reaction with sodium p-chlorophenolate.** In view of the fact that in the first experiments only non-crystallizing viscous oils were obtained, we decided to prepare the corresponding ketone and ketal.

*α-(p-Chlorophenoxy) propyl phenyl ketone* was obtained by heating a solution of 12.2 g of the bromo ketone and 6.8 g of p-chlorophenol in 70 ml of acetone for 6 hrs in the presence of 7.5 g of fused potash. The cooled solution was treated with water to dissolve the KBr, and the obtained yellow oil was extracted with ether; the ether extract was washed with alkali and then dried over $MgSO_4$. After distilling off the ether the residual oil rapidly turned completely crystalline (m. p. 39°). Recrystallization from ethyl alcohol gave 9 g of colorless prismatic crystals with m. p. 40°.

Found %: Cl 13.00, 12.88. $C_{16}H_{15}O_2Cl$. Calculated %: Cl 12.9.

The 2,4-dinitrophenylhydrazone of the ketone was obtained as orange crystals (from ethyl acetate), m. p. 170° (in a sealed capillary).

Found %: N 12.04; Cl 8.04. $C_{22}H_{19}O_5N_4Cl$. Calculated %: N 12.32; Cl 7.81.

*The methyl p-chlorophenyl ketal of ethylbenzoylcarbinol* was obtained by reacting 4 g of the methyllactolide of ethylbenzoylcarbinol with 2.88 g of p-chlorophenol in 25 ml of benzene. The residue with m. p. 39° that deposited the following day was recrystallized from methyl alcohol. We obtained 0.3 g of the cyclodimethyldilactolide of ethylbenzoylcarbinol and 1.5 g of its methyl p-chlorophenyl ketal as colorless crystals with m. p. 154°.

Found %: Cl 11.04, 11.02; $CH_3O$ 9.88, 10.00; act. H 0.98. $C_{17}H_{19}O_3Cl$. Calculated %: Cl 11.5; $CH_3O$ 10.1; act. H 1.

The ketal is stable when kept in the air. When boiled for a long time in alcohol solutions the ketal is completely decomposed to p-chlorophenol and the cyclodimethyldilactolide of ethylbenzoylcarbinol.

*Action of sodium p-chlorophenolate on the α-bromo ketone in methyl alcohol solution.*** To a solution of the sodium chlorophenolate, prepared from 0.5 g of metallic sodium, 20 ml of anhydrous methyl alcohol and 2.8 g of p-chlorophenol, was added 5 g of the bromo ketone. A slight evolution of heat was observed, and NaBr began to precipitate immediately. The mixture was heated to the boil; after cooling the mixture the NaBr was filtered, the methyl alcohol was vacuum-distilled, and the residual oil and crystals were treated with water and then with ether. A noncrystallizing oil was obtained after removal of the ether in vacuo. It was freed from impurities by heating in vacuo at 4 mm to 120°. The residue crystallized rapidly. The substance was recrystallized from ethyl alcohol. M. p. 40°. Yield 66%. Its mixture with α-(p-chlorophenyl) propyl phenyl ketone melted at the same temperature.

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* Done by T. B. Remizova.

** Done by T. B. Remizova.

**e) Reaction with sodium p-nitrophenolate.*** For reaction we took 0.23 g of Na, 10 ml of $CH_3OH$, 1.39 g of p-nitrophenol and 2.27 g of α-bromopropyl phenyl ketone. The reaction mixture was heated for 6 hrs. After the usual treatment an oil was obtained that crystallized only after 5 days, and after recrystallization from ethyl alcohol the crystals melted at 53-54°. Since analysis of the crystals revealed too high a nitrogen content when calculated as the p-nitrophenoxy ketone, the substance was purified further from p-nitrophenol by washing its ether solution with caustic. The α-(p-nitrophenoxy) propyl phenyl ketone purified in this manner, after recrystallization from ethyl alcohol, melted at 56°. Besides a very small amount of p-nitrophenol, no other products were isolated from the mother liquors.

**α-(p-Nitrophenoxy) propyl phenyl ketone** was also prepared by the reaction of p-nitrophenol (2.72 g) with α-bromopropyl phenyl ketone (4.54 g) in acetone (50 ml) solution in the presence of potash (2.76 g). The mixture was heated for 6 hrs, after which water was added to dissolve the NaBr. The obtained heavy oil was extracted with ether, and the ether solution was washed with alkali, then with water, and dried over $MgSO_4$. After distilling off the ether an oil was obtained, which crystallized only after standing for 9 days. Recrystallization from ethyl alcohol gave 3 g of slightly greenish prismatic crystals with m. p. 56°. Their mixture with the substance, obtained in the reaction of sodium p-nitrophenolate with the same bromo ketone in methyl alcohol solution, melted at the same temperature.

Found %: C 67.31; H 5.39; N 4.86, 5.38. $C_{16}H_{15}O_4N$. Calculated %: C 67.37; H 5.26; N 4.91.

The 2,4-dinitrophenylhydrazone of the ketone was recrystallized from ethyl acetate. M. p. 210° in a sealed capillary.

Found %: N 15.20. $C_{22}H_{19}O_7N_5$. Calculated %: N 15.05.

**Preparation of methyl p-nitrophenyl ketal of ethylbenzoylcarbinol.** To a solution of 3 g of p-nitrophenol in 25 ml of dry benzene was added 4 g of the methyllactolide of ethylbenzoylcarbinol. The next day the deposited crystals were recrystallized from methyl alcohol; however, in this case the substance underwent considerable decomposition with the formation of p-nitrophenol and the cyclodimethyldilactolide of ethylbenzoylcarbinol (IV) with m. p. 240° [6]. Subsequently the compound was recrystallized from benzene. We obtained 1.98 g of colorless coarsely crystalline substance with m. p. 122°.

Found %: C 64.28, 64.30; H 6.21, 6.23; N 4.57, 4.54; $OCH_3$ 9.65, 9.57. $C_{17}H_{19}O_5N$. Calculated %: C 64.35; H 6.00; N 4.42; $OCH_3$ 9.75.

## II. Reaction of α-Bromoisopropyl Phenyl Ketone with Sodium Arylates**

**a) Reaction with sodium β-naphtholate.***** To a solution of the sodium naphtholate, prepared from 1.01 g of Na and 6.4 g of β-naphthol in 25 ml of methyl alcohol, was added 10 g of the bromo ketone in 5 ml of methyl alcohol. Reaction in the cold was complete in 3 hrs. After the usual treatment we obtained 7.1 g of the methyl β-naphthyl ketal of dimethylbenzoylcarbinol, which after two recrystallizations from methyl alcohol had m. p. 105°. Yield 50%.

Found %: C 78.34, 78.37; H 6.90, 6.96; $CH_3O$ 9.30, 9.24; act. H 1.08, 1.06. $C_{21}H_{22}O_3$. Calculated %: C 78.26; H 6.83; $OCH_3$ 9.63; H 1.

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* Done by T. B. Remizova.

** The reaction with sodium phenolate was described earlier [3].

*** Done by O. A. Netsetskaya.

After all of the substance with m. p. 105° had crystallized out, and all of the mother liquor had been evaporated, we obtained a very small amount of crystals with m. p. 185-186°, identified as the anhydro dimer of dimethylbenzoylcarbinol [7].

The methyl β-naphthyl ketal of dimethylbenzoylcarbinol was also obtained from 1.32 g of β-naphthol and 1.66 g of the methyllactolide of the indicated keto alcohol in benzene solution. The crystals deposited only after the benzene had been vacuum-distilled. Recrystallization from benzene gave a substance with m. p. 104-105°. Its mixture with the ketal, obtained from the α-bromo ketone, melted at the same temperature. The anhydro dimer of dimethylbenzoylcarbinol was isolated from the mother liquor residues.

b) Reaction with sodium α-naphtholate.* The experiment was run under exactly the same conditions as in the case of sodium β-naphtholate. Reaction was complete in 3 hrs. After vacuum-distillation of the methyl alcohol the residue was poured into a crystallizing dish, and after 3 days the whole had solidified to a dark-brow mass. It was dissolved in hot methyl alcohol. On cooling the solution, first tetragonal and then bead-like crystals deposited. All of the crystals melted at the same temperature of 102-103°; the color of the compound was pale-orange.. Coarse thick plates began to deposit from the last mother liquor, which after recrystallization from methyl alcohol had m. p. 86-88° (in a sealed capillary, 89-91°). Total yield of all of the crystals was 7.7 g.

Analysis of crystals with m. p. 102-103°. Found %: C 78.03, 77.98; H 6.99, 7.00; $OCH_3$ 9.76, 9.80; act. H 1.09.

Analysis of crystals with m. p. 86-88°. Found %: C 78.27; H 7.01; $OCH_3$ 9.42. $C_{21}H_{22}O_3$. Calculated %: C 78.26; H 6.83; $OCH_3$ 9.63; act. H 1.

Both types of crystals correspond to the same compound — the methyl α-naphthyl ketal of dimethylbenzoylcarbinol. Their mixtures in different proportions melted sharply at 102-103°. For comparison the ketal was also prepared by the reaction of α-naphthol with the methyllactolide of ethylbenzoylcarbinol, using 1.32 g of α-naphthol and 1.66 g of the methyllactolide in benzene solution. After vacuum-distillation of the benzene without heating the residue was poured into a crystallizing dish. Coarse crystals began to appear on the following day; after purification with methyl alcohol they melted at 103°; their mixture with the ketal, obtained from the bromo ketone, melted at the same temperature. Gradually the entire content of the crystallizing dish became filled with these crystals; however, subsequently the appearance of α-naphthol, colored pink, began to be observed, and in the same places also needle-like crystals with m. p. 185-186° (anhydro dimer of the keto alcohol [7]). After several days the crystals with m. p. 103° disappeared, and the whole had migrated into α-naphthol and the anhydro dimer.

c) Reaction with sodium p-nitrophenolate.** To a solution of sodium p-nitrophenolate, prepared from 0.5 g of sodium, 3 g of p-nitrophenol and 20 ml of methyl alcohol, was added 5 g of α-bromoisopropyl phenyl ketone. After removal of the methanol in vacuo the residue was recrystallized from ethyl alcohol; crystals with m. p. 96-97° were obtained. Yield 28%.

Found %: C 67.09, 67.18; H 5.53, 5.39; N 4.84. $C_{16}H_{15}O_4N$. Calculated %: C 67.38; H 5.26; N 4.91.

The α-nitrophenoxypropyl phenyl ketone was also obtained by running the reaction in acetone; a mixture of 5 g of the bromo ketone, 3.06 g of p-nitrophenol, 3 g of potash and 40 ml of acetone was heated until the test for halogen was negative. The reaction mixture was worked up in the usual manner to yield crystals with m. p. 97°. Their mixture with the substance, obtained in methyl alcohol, also melted at 97°. Yield 42%.

For comparison we prepared the methyl p-nitrophenyl ketal of dimethylbenzoylcarbinol. To a solution of 3.97 g of p-nitrophenol in 30 ml of benzene was added in drops a solution of 5.48 g of the methyllactolide in 7 ml of benzene with stirring, which was continued until all of the p-nitrophenol had dissolved. The solution was let stand for a day at room temperature. The next day the solution was chromatographed through a column packed with $Al_2O_3$, having a height of 8.5 cm. Three fractions were taken. The 1st fraction was pure benzene, while from the 2nd, and partially from the 3rd fraction, after vacuum-distillation of the benzene without heating, a yellow, extremely viscous oil was isolated, which was washed with ether to remove traces of benzene, and the ether was removed in vacuo. The yield, calculated as the ketal, was 50%.

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* Done by O. A. Netsetskaya.

** Done by G. A. Ugolnikova.

Found %: C 64.42, 64.18; H 6.23, 6.30; N 4.53. M 321.6. $C_{17}H_{19}O_5N$. Calculated %: C 64.35; H 6.00; N 4.42. M 317.3.

The substance is easily hydrolyzed with alkali in the presence of alcohol and is decomposed when heated with alcohol.

A solution of 1.04 g of the ketal in 20 ml of ethyl alcohol was heated for 3 hrs, after which the alcohol was distilled off, the residue dissolved in ether, the ether extract washed with water and alkali to remove p-nitrophenol, and then it was dried over fused $MgSO_4$. Removal of the ether by distillation left an oil, from which the 2,4-dinitrophenylhydrazone was prepared, which after recrystallization melted at 144-145° in a sealed capillary. The mixed melting point with the authentic 2,4-dinitrophenylhydrazone of dimethylbenzoylcarbinol, melting at 145-146°, was not depressed.

d) Reaction with sodium 3,4-xylenolate.* To a colorless solution of the calculated amount of sodium xylenolate in 25 ml of methyl alcohol was added a solution of 10 g of the bromo ketone in 5 ml of methanol. The solution turned slightly yellow, but when all of the bromo ketone had been added the yellow color disappeared, and NaBr began to deposit. Reaction was complete in 2 hrs. Vacuum-distillation of all of the alcohol, separation of the NaBr, and evaporation of the alcohol residues, gave a completely colorless solid as residue. A good recrystallization solvent for the solid proved to be either aqueous or anhydrous methyl alcohol; in the first case tiny needles were obtained, and in the second – short, stout, transparent rods, collecting as aggregates. After one recrystallization the isolated methyl 3,4-xylenyl ketal of dimethylbenzoylcarbinol had m. p. 103-104°.

Found %: C 75.97, 75.92; H 7.85, 7.90; $OCH_3$ 10.45, 10.70; act. H 0.98. $C_{19}H_{24}O_3$. Calculated %: C 76.00; H 8.00; $OCH_3$ 10.33; act. H 1.

The crystals that deposited from the motherliquor were again recrystallized from methyl alcohol, but first they were allowed to stand in the solution overnight under the solvent. The next morning the crystals had disappeared, and after several days an entirely different type of crystals – tiny tetragons – had deposited. M. p. 185-186°; their mixture with the anhydro dimer of dimethylbenzoylcarbinol melted at the same temperature. We obtained 5.75 g of the ketal and 1.0 g of the anhydro dimer of the keto alcohol.

The same ketal was also obtained by reacting 1.66 g of the methyllactolide of the same keto alcohol with 1.13 g of 3,4-xylenol. The reaction was run in the usual manner. The crystals melted at 103-104°, and did not give a melting point depression when mixed with the ketal, obtained in the preceding experiment. After 3 days the entire mass had changed to a hard crystalline substance with m. p. 103°. However, if the crystals were allowed to stand in the crystallizing dish without purification, then by the next day they had changed to a light-colored mobile liquid, from which the anhydro dimer of the keto alcohol, with m. p. 185-186°, gradually began to deposit as tiny tetragonal crystals.

## III. Reaction of α-Bromoethyl Phenyl Ketone with Sodium p-Nitrophenolate**

To a solution of sodium p-nitrophenolate, prepared from 0.54 g of sodium, 3.26 g of p-nitrophenol and 40 ml of methyl alcohol, was added 5 g of the bromo ketone. After removal of the methyl alcohol the isolated precipitate was washed with ether. The ether extract was worked up to give α-(p-nitrophenoxy)ethyl phenyl ketone; when recrystallized from ethyl alcohol it was obtained as slender needles with a pale yellow color. M. p. 82-83°. Yield 25%.

Found %: C 66.85, 66.41; H 5.14, 4.85. N 5.30. $C_{15}H_{13}O_4N$. Calculated %: C 66.42; H 4.80; N 5.16.

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* Done by O. A. Netsetskaya.

** Done by G. A. Ugolnikova.

The same compound was also obtained when the reaction was run in acetone in the presence of potash. M. p. 82-83°. Its mixture with the p-nitrophenoxy ketone, obtained in methyl alcohol solution, melted at the same temperature.

Attempt to prepare the methyl p-nitrophenyl ketal of methylbenzoylcarbinol. To a mixture of 6 g of p-nitrophenol and 30 ml of benzene was added 6 g of the methyllactolide of methylbenzoylcarbinol in drops. The p-nitrophenol crystals dissolved with self-heating of the solution to 40°. The next day the benzene was removed in vacuo, and the residue – a yellow oil – began to crystallize gradually. The isolated crystals, after pressing on a porous plate, melted at 110-112°, and did not depress the melting point with p-nitrophenol. The next day the reaction product had turned to a tar. Washing the tar with either benzene or ether left crystals with m. p. 196-198°, which after recrystallization from methanol melted at 244.5-245.5° (the melting point of the cyclodimethyldilactolide of methylbenzoylcarbinol [6]).

An attempt to chromatograph a benzene solution of the reaction product on $Al_2O_3$ led to the same result. The fractions isolated after chromatographing were found to contain crystals of the cyclodimethyldilactolide of methylbenzoylcarbinol.

### IV. Reaction with α-Bromobutyl Phenyl Ketone*

a) The reaction of α-bromo ketone with sodium phenolate in methyl alcohol was described earlier [3]. The reaction of the α-bromo ketone with phenol in acetone in the presence of potash gave α-phenoxyvalerophenone with m. p. 45° (from ethyl alcohol).

Found %: C 80.05, 80.26; H 7.14, 7.16. M 247. $C_{17}H_{18}O_2$. Calculated %: C 80.31; H 7.14; M 254.

α-Phenoxyvalerophenone was characterized as the 2,4-dinitrophenylhydrazone with m. p. 55-56°.

Found %: N 13.05, 12.95. $C_{23}H_{22}N_4O_5$. Calculated %: N 12.90.

b) Reaction with sodium m-cresolate. 1. In methyl alcohol. 10 g of α-bromobutyl phenyl ketone was added in drops to a solution of 0.95 g of sodium and 4.48 g of m-cresol in 40 ml of methanol. The reaction was run in the usual manner for the preparation of ketals. Recrystallization from methanol gave the methyl m-cresyl ketal of propylbenzoylcarbinol as crystals with m. p. 106°.

Found %: C 75.86, 75.74; H 8.13, 7.97; $OCH_3$ 10.16; H act. 0.94. $C_{19}H_{24}O_3$. Calculated %: C 76.00; H 8.00; $OCH_3$ 10.33; H act. 1.

2. In acetone. A mixture of 10 g of α-bromobutyl phenyl ketone, 4.48 g of m-cresol and 5.72 g of potash in 40 ml of acetone was heated under reflux until the Beilstein test for halogen was negative. After the usual treatment and recrystallization from ethanol we obtained the α-(m-cresoxy)butyl phenyl ketone with m. p. 56°.

Found %: C 80.49, 80.52; H 7.69, 7.62. $C_{18}H_{20}O_2$. Calculated %: C 80.61; H 7.46.

The 2,4-dinitrophenylhydrazone of the ketone had m. p. 127°.

Found %: N 12.57. $C_{24}H_{24}O_5N_4$. Calculated %: N 12.50.

### V. Preparation of α-Phenoxyisobutyl Phenyl Ketone**

The reaction was run using 6.5 g of α-bromoisobutyl phenyl ketone, 2.92 g of phenol, 5 g of potash and 40 ml of acetone. After the usual treatment and recrystallization from alcohol the obtained ketone had m. p. 96-97°.

Found %: C 80.41, 80.41; H 7.33, 7.38. M 240. $C_{17}H_{18}O_2$. Calculated %: C 80.31; H 7.14. M 254.

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* Done by G. A. Ugolnikova.

** Done by G. A. Ugolnikova.

## SUMMARY

**Support was obtained for the earlier made observation that it is possible for the reaction of sodium arylates with α-bromoalkyl phenyl ketones to proceed in two directions in methyl alcohol solution – in the direction of forming the α-aryloxy ketone and that of forming the methyl aryl ketal of the α-keto alcohol. The nucleophilic properties of the arylate and the structure of the α-bromo ketone determine which of the indicated directions predominates.**

## LITERATURE CITED

[1] T. I. Temnikova and Myukhyurdari, J. Gen. Chem. 24, 1819 (1954).*

[2] C. Bradsher and R. Rosher, J. Am. Chem. Soc. 61, 1524 (1939).

[3] G. A. Ugolnikova, J. Gen. Chem. 27, 343 (1957). *

[4] T. I. Temnikova, Transactions of the Kiev Society for 1952 (Izd. AN SSSR, 1953), 266.

[5] G. A. Ugolnikova, Bull. Leningrad State Univ. 10, 106 (1957).

[6] T. I. Temnikova and A. I. Spasskova, J. Gen. Chem. 16, 1681 (1946).

[7] A. E. Favorsky and N. Mandryka, J. Russ. Chem. Soc. 44, 1387 (1912).

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# SYNTHETIC INVESTIGATIONS IN THE FIELD OF POLYENES

## XIII. SYNTHESIS OF POLYENIC KETONES BY PYROLYSIS OF ACETOACETATES OF TERTIARY ACETYLENIC CARBINOLS

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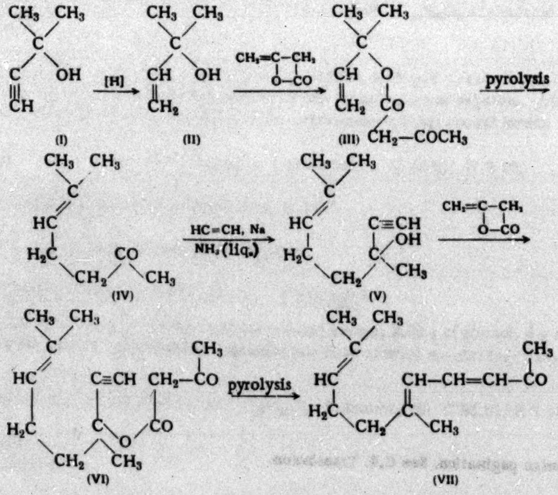
N. A. Preobrazhensky

It is well known that acetoacetic ester decomposes on heating, in the presence of bases, into alcohol and dehydracetic acid [1, 2]. Heating acetoacetic ester with α,β-unsaturated alcohols in the presence of alkaline catalysts gives rise to the formation of unsaturated ketones [3]. This reaction may be regarded as a transesterification with an intramolecular rearrangement in the resultant acetoacetates of ethylenic alcohols. In fact, under conditions of pyrolysis, acetoacetates of unsaturated alcohols also lose carbon dioxide and form γ,δ-unsaturated ketones [4, 5]. The use of the α-chloro-substituted derivative of acetoacetic ester in a similar transformation gave γ,δ-unsaturated monochloroketones, and treatment of the latter with pyridine led to the formation of diene ketones [6]. Recently it has been shown by Lacey [7] and by ourselves [8, 9] that a similar intramolecular rearrangment with the splitting off of carbon dioxide and formation of diene ketones also takes place during pyrolysis of acetoacetates of tertiary acetylenic alcohols, while Naves [10] found that heating acetylenic tertiary carbinols with acetoacetic ester also gives rise to the formation of diene ketones.

The pyrolytic decarboxylation and isomerization of acetoacetates of ethylenic and acetylenic alcohols have been used by us in the synthesis of pseudoionone (VII) [8, 9] in accordance with the following scheme:



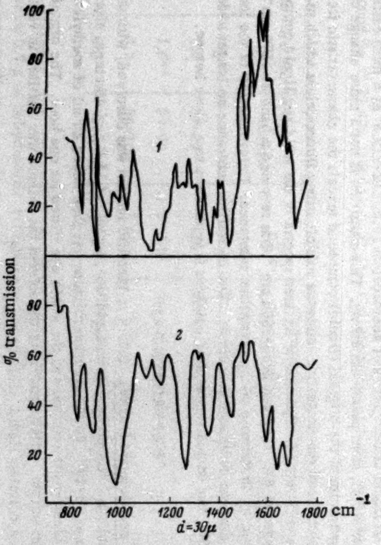


Fig. 1. Infrared absorption spectra.
1) Ketone isomeric with pseudoionone (fraction No. 3 of the products of pyrolysis of dehydrolinalool acetoacetate), 2) pseudoionone (fraction No. 5 from the same experiment).

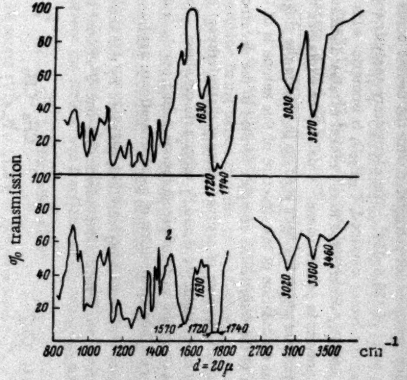
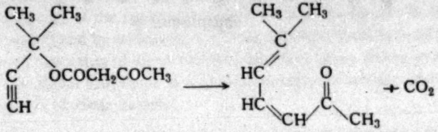


Fig. 2. Infrared absorption spectra.
1) Dimethylpropynylcarbinol acetoacetate (liquid), 2) its crystalline isomer (m.p. 45-49.5°).

To explain the mechanism of this transformation, Lacey and Naves have suggested that there is formed an intermediate cyclic complex which decomposes with the evolution of carbon dioxide, the resultant molecule being stabilized in the form of an allene compound. On fractionating in vacuo the products formed on heating of the acetoacetate of dehydrolinalool (VI) to 180° we have obtained fractions which contained dehydrolinalool, dehydracetic acid and carbonyl compounds. In contrast to the results of Naves, we were unable to confirm the formation of allenic ketones during the decomposition of the acetoacetate of dehydrolinalool (VI). Examination of ultraviolet and infrared absorption spectra (Fig. 1) of fractions boiling at temperatures below the boiling point of pseudoionone (fraction No. 3, see Experimental) indicated the presence of a compound in which, unlike in pseudoionone (and in ionones), the carbonyl group is not conjugated with the double bonds ($\nu$ 1710 $cm^{-1}$). The semicarbazone of this ketone had a melting point of 133.5-134°. The elementary analysis corresponded to the formula $C_{14}H_{23}ON_3$; from this it follows that the ketone obtained, $C_{13}H_{20}O$, is isomeric with pseudoionone. Catalystic hydrogenation of the ketone over a partially deactivated Raney nickel catalyst indicated the presence of only two double bonds instead of the three present in pseudoionone. This may be explained on the assumption that the ketone is a cyclic one in which the double bond which has been used up in closing the ring, is conjugated in pseudoionone with the carbonyl group. The final elucidation of the structure of this ketone is of interest from the point of view of the mechanism of stabilization of the transitional complex formed in the decarboxylation step.

Lacey views the pyrolytic transformations of acetoacetates of dialkylethynyl carbinols into dienones as a reaction which is catalyzed by p-toluenesulfonic acid and by other acid catalysts. However, we have found that whereas in the absence of acid catalysts the yield of pseudoionone during pyrolysis of dehydrolinalool acetoacetate was 62 %, no increased yield was obtained on addition of p-toluenesulfonic acid.

By heating the acetoacetate of dimethylethynylcarbinol, prepared by the action of diketene on the carbinol, to 160° we effected its transformation into 6-methylheptadiene-3,5-one-2 without the aid of p-toluenesulfonic acid, in contrast to the findings of Lacey:



However, it was found that the liquid dimethylethynyl acetoacetate (b.p. 112-112.5° at 6 mm) easily changes into a crystalline substance (m.p. 49-49.5°, from petroleum ether). This transition is not a mere change of the state of aggregation. The Raman spectrum of the original (liquid) compound reveals the characteristic frequency of the triple bond (2112 $cm^{-1}$). Solutions of the crystalline substance exhibit strong fluorescence which makes the investigation of its Raman spectrum difficult. Comparison of infrared spectra of the solid and liquid compounds, at present studied only over the ranges of 800-1600 and 2700-3600 $cm^{-1}$, has revealed a band at 1570 $cm^{-1}$ (strongly displaced frequency of a double bond ?) in the case of the crystalline substance. Determination of the molecular weight gives no reasons to suppose that the compound is a dimer. The crystalline substance no longer undergoes the isomerizations on heating to 180°, but on addition of acid catalysts it isomerizes to a diene ketone.

## EXPERIMENTAL

1. Dimethylethynylcarbinol acetoacetate (liquid). 0.05 g of metallic sodium was dissolved, with stirring, in 12.6 g of dimethylethynylcarbinol (I), followed by dropwise addition, at 10°, of 14.8 g of diketene, after which the mixture was stirred for 16 hours at 18-20°. To the reaction mixture was then added 40 ml of methylene chloride and 30 ml of saturated sodium bicarbonate solution and the whole was stirred for one hour. The organic layer was separated and dried over sodium sulfate. After removal of the solvent the residue was distilled in vacuo. The acetoacetate of (I) was obtained as a colorless liquid, yield 22.3 g (88.5 %).

B. p. 93-94° at 8 mm, $d_4^{20}$ 1.0204, $n_D^{20}$ 1.4449, $MR_D$ 43.81. $C_9H_{12}O_3|\equiv$ Calculated 43.43.

The crystalline isomer of the acetoacetate of (I) was obtained quantitatively by dissolving the latter in ether, scratching the walls of the vessel and gradually evaporating the solvent, or by introducing a trace of the crystalline substance.

M.p. 49-49.5° (from petroleum ether). Mol. wt. (cryoscopic) 166. $C_9H_{12}O_3$. Calculated Mol. wt. 168.

2. 6-Methylheptadiene-3,5-one-2. 11.2 g of acetoacetate of (I) (liquid) was heated in a current of nitrogen at 170-180° for 3 hours, cooled and distilled in vacuo. A faintly yellow liquid was obtained, yield 4.2 g (50.7 %).

B. p. 85-86° at 10 mm, $n_D^{20}$ 1.5291, $\lambda_{max}$ 290 mμ, ε 27600.

3. Dimethylvinylcarbinol acetoacetate (III) was obtained as a colorless liquid from 31.1 g of dimethylvinyl carbinol [11] and 36.2 g of diketene under conditions similar to those used in Experiment No. 1. Yield 46.7 g (76%).

B. p. 97-98° at 10 mm, $d_4^{20}$ 0.9886, $n_D^{20}$ 1.4386, $MR_D$ 45.23. $C_9H_{14}O_3$╒. Calculated 44.96.

Found %: C 63.26; H 8.77; $C_9H_{14}O_3$. Calculated %: C 63.53; H 8.23.

4. 2-Methylheptene-2-one-6 (IV). 42.5 g of (III) was heated in a current of nitrogen at 140-160° for 2 hours and subsequently distilled in vacuo. Yield, 22.3 g (71 %).

B. p. 68-70° at 5 mm, $d_4^{20}$ 0.8538, $n_D^{20}$ 1.4404, $MR_D$ 38.96. $C_8H_{14}O$╒ Calculated 38.69.

5. Dehydrolinalool (V). 2.7 g of metallic sodium was dissolved in 150 ml of liquid ammonia at a temperature of -50 to -60°, a current of acetylene being passed into the mixture at such a rate as to prevent the solution from assuming a bluish color. When all the sodium dissolved, stirring and passage of acetylene was continued for another 20-30 minutes after which 20.1 g of 2-methylheptene-2-one-6 was added dropwise. The mixture was stirred for another 3-4 hours with slow passage of acetylene. At the end of this period the cooling was stopped, 12 g of ammonium chloride added and the ammonia removed. To the reaction mixture was added 50 ml of methylene chloride and 50 ml of water, the organic layer was removed and the aqueous layer was again extracted with 50 ml of the same solvent. The combined extracts were washed with saturated sodium chloride solution and dried over sodium sulfate. After removing the solvent the residue was fractionated in vacuo. Yield 17.9 g (74 %).

B. p. 98-100° at 7 mm, $d_4^{20}$ 0.884, $n_D^{20}$ 1.4622, $MR_D$ 47.15. $C_{10}H_{16}O$╒ |≡ Calculated 47.43.

6. Dehydrolinalool acetoacetate (VI). To 17.9 g of dehydrolinalool (V) was added 0.1 g of metallic sodium and the mixture was stirred until the latter dissolved completely. The mixture was then cooled to 10° and 7.8 g of diketene was added dropwise. Stirring was continued for 2-3 hours at 10-12° after which the mixture was allowed to stand for 12 hours at 17-18°. The subsequent treatment was similar to that followed in Experiment No. 3. Yield, 20.1 g (72.1 %).

B. p. 78-80° at 0.1 mm, $d_4^{20}$ 0.9879, $n_D^{20}$ 1.4662, $MR_D$ 66.22. $C_{14}H_{20}O_3$ ╒ |≡ Calculated 66.05.

Found %: C 71.42; H 8.64. $C_{14}H_{20}O_3$. Calculated %: C 71.18; H 8.47.

| Fraction No. | Weight g | Boiling point | $n_D^{20}$ | Characteristic absorption band | | $H_2$ absorbed per mole of compound | 2,4-Dinitrophenylhydrazone | |
|---|---|---|---|---|---|---|---|---|
| | | | | $\lambda_{max}$ | $E_{1\,cm}^{1\%}$ | | m.p. | N found (%) |
| 3 | 1.9 | 83-89° | 1.4820 | No characteristic band | | 1.78 | 75-77° | 15.17* |
| 4 | 1.6** | 90-95 | 1.4916 | No characteristic band | | – | – | – |
| 5 | 6.2 | 96-100 | 1.5312 | 290 | 1120 | 2.92 | 135-136 | 14.83*** |
| 6 | 3.9 | 100-108 | 1.5316 | 290 | 1180 | – | – | – |

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* Semicarbazone, m.p. 133.5-134°. Found %: N 16.51. $C_{14}H_{23}ON_3$. Calculated %: N 16.85.

** Contains 0.7 g of dehydracetic acid. M. P. 108-109°.

*** Dinitrophenylhydrazone, $C_{19}H_{24}N_4O_4$. Calculated %: N 15.05.

7. Pseudoionone and its isomeric ketone. 20.1 g of (VI) was heated for 3 hours at 170-180° in a current of nitrogen, cooled and fractionated in vacuo. At a residual pressure of 2 mm 6 fractions were obtained. The first two fractions (combined weight 2.1 g) contained dehydrolinalool with a small amount of carbonyl compounds; the other four fractions had the chracteristics given in the table. Yield of pseudoionone (Fractions No. 5 and 6) was 10.1 g (61.8 %), based on (VI).

Characteristic frequencies in the 800-1800 $cm^{-1}$ range of infrared spectrum; fraction No. 3 (cyclic ketone): 850, 910, 970, 1000, 1030, 1140, 1180, 1250, 1270, 1330, 1370, 1390, 1450, 1520, 1545, 1580, 1650, 1660, 1680, 1710 ($cm^{-1}$). Fraction No. 5 (pseudoionone): 830, 892, 980, 1110, 1170, 1260, 1360, 1442, 1591, 1634, 1670, 1680 ($cm^{-1}$).

## SUMMARY

1. A complete synthesis of pseudoionone has been carried out by pyrolytic transformations of tertiary ethylenic and acetylenic alcohols.

2. The pyrolytic transformation of dehydrolinalool acetoacetate involves the decarboxylation and isomerization of the transitional complex into a triene ketone (pseudoionone) and partly into a cyclic ketone in which the carbonyl group is not conjugated with the double bonds.

3. Dimethylethynyl carbinol acetoacetate is easily transformed into an isomeric crystalline compound which shows different behavior during pyrolysis and has a different infrared absorption spectrum.

## LITERATURE CITED

[1] F. Arndt and P. Nachtwey, Ber. 57, 1489 (1924).

[2] F. Arndt, B. Eistert, H. Scholz and E. Aron, Ber. 69, 2373 (1936).

[3] Caroll, J. Chem. Soc. 1940, 704, 1266; 1941, 507.

[4] W. Kimel and A. Cope, J. Am. Chem. Soc. 65, 1992 (1943).

[5] U. S. Pat. 2658911; 2658484; Ch. A. 49, 1100 (1955); 48, 2763 (1954).

[6] Ch. Tavel, Helv. Chim. Acta, 33, 1266 (1950).

[7] R. N. Lacey, J. Chem. Soc. 1954, 827.

[8] G. I. Samokhvalov, M. A. Miropolskaya and N. A. Preobrazhensky, Proc. Acad. Sci. USSR, 107, 103 (1956).*

[9] G. I. Samokhvalov and M. A. Miropolskaya and N. A. Preobrazhensky, Authors' Cert. No. 103776 (1955).

[10] Y. R. Naves, C. r. 240, 1437 (1955); Y. R. Naves, and P. Ardizio, Bull. Soc. Chim. 1955, 1479; Y. R. Naves and P. Ardizio, Bull. Soc. Chim. 1956, 672.

[11] I. N. Nazarov, V. N. Rakcheeva, V. Ya. Raigorodskaya and I. N. Azerbayev, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 305.

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* Original Russian pagination. See C.B. Translation.

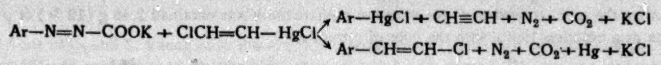
# INTERACTION OF SALTS OF ARYLAZOCARBOXYLIC ACIDS WITH CIS- AND TRANS-β-CHLOROVINYLMERCURICHLORIDES

O. A. Reutov and E. M. Fedneva

As has been shown by A. N. Nesmeyanov and one of us [1], salts of arylazocarboxylic acid react with corrosive sublimate to give organo-mercury compounds.

$$Ar{-}N{=}N{-}COOK + HgCl_2 \rightarrow Ar{-}HgCl + N_2 + CO_2 + KCl$$

In the present work we have studied the reactions of potassium phenyl- and p-tolylazocarboxylates with adducts of corrosive sublimate to acetylene, i.e., β-chlorovinylmercurichlorides. These reactions proceed in two directions. On the one hand, β-chlorovinylmercurichlorides react in the same way as the complex of mercuric chloride with acetylene, giving rise to the formation of an arylmercurichloride, acetylene, nitrogen, carbon dioxide and potassium chloride. On the other hand, they also react as true organo-metallic compounds, the products of the reaction being ω-chlorostyrene, nitrogen, carbon dioxide, metallic mercury and potassium chloride.



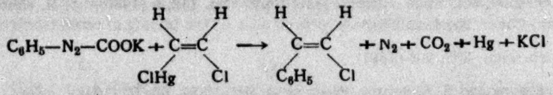
$$Ar{-}N{=}N{-}COOK + ClCH{=}CH{-}HgCl \begin{cases} \rightarrow Ar{-}HgCl + CH{\equiv}CH + N_2 + CO_2 + KCl \\ \rightarrow Ar{-}CH{=}CH{-}Cl + N_2 + CO_2 + Hg + KCl \end{cases}$$

In these reactions is manifest the dual reactivity of β-chlorovinylmercurichlorides which is so characteristic of all compounds of a quasi-complex character [2].

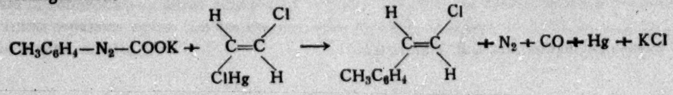
By the interaction of potassium phenylazocarboxylate with trans-β-chlorovinylmercurichloride there was formed trans-ω-chlorostyrene (b.p. 89° [18 mm], 199° [758 mm], $n_D^{15}$ 1.5802, $d_4^{15}$ 1.1115), which was identical with that described in the literature [3].

Reaction of potassium phenylazocarboxylate with cis-β-chlorovinylmercurichloride leads to the formation of ω-chlorostyrene which has different characteristics, namely, b.p. 60-64° (18 mm), $n_D^{15}$ 1.5763, $d_4^{15}$ 1.1623.

Since, according to the authors of [4], electrophilic and free-radical substitutions in organo-metallic derivatives of β-chlorovinyl take place with the conservation of the spatial configuration of the chlorovinyl group, it may be assumed that the chlorostyrene in question is the cis-isomer.



Interaction of potassium p-tolylazocarboxylate with trans-β-chlorovinylmercurichloride gives p-methyl-ω-chlorostyrene (b.p. 99-101° [14 mm], $n_D^{27}$ 1.5660), which is identical with that described in the literature [5]. Data on the configuration of this compound are absent in the literature, but in view of the fact that this isomer is formed from trans-β-chlorovinylmercurichloride it may be assumed, following the Nesmeyanov-Borisov rule, that it has the trans-configuration.



## EXPERIMENTAL

Interaction of potassium phenylazocarboxylate with trans-β-chlorovinylmercurichloride. To a solution of 35.7 g (0.12 mole) of trans-β-chlorovinylmercurichloride in 200 ml of anhydrous acetone was added, with vigorous stirring, in the cold, 29.5 g (0.157 mole) of potassium phenylazocarboxylate over 40 minutes. The reaction mixture darkened rapidly (liberation of metallic mercury) and became warm. At the end of the addition of the potassium salt the mixture was stirred for another half hour. The precipitate which separated (KCl, $KHCO_3$, Hg) was filtered off (filtrate I). Acetone was removed from filtrate (I) after which the residue was shaken with a small amount of ether and filtered off (filtrate II). The residue on the filter was phenylmercurichloride, which after recrystallization from acetone, had a melting point of 252°. Yield, 7.0 g (18.5%). Most of the ether was removed from filtrate (II) and the residue was distilled in vacuo. The distillate — a colorless liquid with an odor of hyacinth — was found to be trans-ω-chlorostyrene. Yield 2.1 g (12 %, calculated on the chlorovinylmercurichloride).

B. p. 89° (18 mm), 199° (758 mm), $n_D^{15}$ 1.5802, $d_4^{15}$ 1.1115. As given [3] : b.p. 89° (17.5 mm), 199-199.2° (760 mm), $n_D^{15}$ 1.5808, $d_4^{15}$ 1.1122.

Found %: C 69.19; H 5.25. $C_8H_7Cl$. Calculated %: C 69.37; H 5.10.

Interaction of potassium phenylazocarboxylate with cis-β-chlorovinylmercurichloride. The reaction between 31.3 g of cis-β-chlorovinylmercurichloride and 28 g of potassium phenylazocarboxylate was carried out under the same conditions as those used in the foregoing experiment. By similar subsequent treatment of the reaction mixture there was obtained 1.8 g of ω-chlorostyrene (12%) in the form of a colorless liquid having a hyacinth odor and being easily soluble in acetone, ether and chloroform.

B.p. 194-196° (760 mm), 60-64° (17-18 mm), $n_D^{18}$ 1.5763, $d_4^{18}$ 1.1623.

Found %: C 69.41; H 5.05. $C_8H_7Cl$. Calculated %: C 69.37; H 5.10.

Interaction of potassium p-tolylazocarboxylate with trans-β-chlorovinylmercurichloride. 32.4 g (0.160 mole) of the potassium salt and 40 g (0.134 mole) of trans-β-chlorovinylmercurichloride were reacted under the usual conditions. After the usual treatment of the reaction mixture there was obtained 2.45 g (12 %) of p-methyl-ω-chlorostyrene as a colorless liquid with the odor of citrus fruit.

B. p. 99-101° (14 mm), $n_D^{27}$ 1.5660. As given [5]: b.p. 99-102° (14 mm), $n_D^{26.8}$ 1.5635.

Found %: C 71.20; H 5.95. $C_9H_9Cl$. Calculated %: C 70.80; H 5.95.

## SUMMARY

1. The authors have demonstrated the formation of ω-chlorostyrenes resulting from the interaction of salts of arylazocarboxylic acids with β-chlorovinylmercurichlorides.

2. The geometrical configuration of the ω-chlorostyrenes has been discussed.

## LITERATURE CITED

[1] A. N. Nesmeyanov and O. A. Reutov, Bull Acad. Sci. USSR, Div. Chem. Sci. 1948, 316.

[2] A. N. Nesmeyanov, Sci. Trans. Moscow State Univ. No. 132, 5 (1950); A. N. Nesmeyanov and M.I. Kabachnik, J. Gen. Chem. 25, 41 (1955).*

[3] H. Biltz, Lieb. Ann. 296, 266 (1897).

[4] A. N. Nesmeyanov and A. E. Borisov, Proc. Acad. Sci. USSR, 60, 67 (1948).

[5] Auwers, Hesenland, Lieb. Ann. 352, 278 (1807).

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# IMINES OF DI- AND POLYKETONES

## I. 2-PHENYLINDANDIONE-1,3

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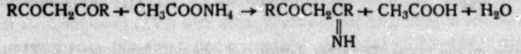
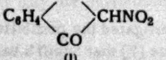
Ketimines are rather unstable compounds and for this reason have been investigated comparatively little [1]. They are usually prepared by heating ketones with ammonia in a sealed tube, or by passing the vapor of the ketone and ammonia over a catalyst [2]. Recently, Balandin and Vasyunina have shown [1] that simple ketimines are easily prepared by catalytic splitting off of hydrogen from the corresponding primary amines.

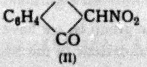
Preparation of monoimines of β-diketones is easy, especially by heating the latter with excess ammonium acetate in the presence of a small amount of glacial acetic acid. Under these conditions one of the keto groups of β-diketones easily undergoes transformation into the ketimino group:



$$RCOCH_2COR + CH_3COONH_4 \rightarrow RCOCH_2\underset{\underset{NH}{\|}}{C}R + CH_3COOH + H_2O$$

Recently one of us and E. Vanag have shown [3] that under these conditions 2-nitroindandione-1,3 (I) gives the monoimine (II). In contrast to many other ketimines, nitroindandione ketimine proved to be very stable, a fact which was ascribed to the existence in its molecule of two intramolecular hydrogen bonds (III). This would also explain the more intense color of the imine as compared with that of the starting nitroindandione.


(I)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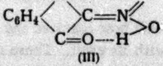
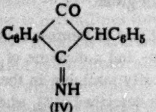

(III)

In view of this it was of interest to extend the investigation to several other 2-substituted indandiones-1,3. For the start we chose 2-phenylindandione-1,3. This compound is easily accessible and has recently become important as a valuable blood anticoagulant. On heating it with ammonium acetate in glacial acetic acid there is formed, in almost quantitative yield, the red phenylindandione imine (IV). (Phenylindandione itself is colorless, but forms colored salts). The reaction occurs so easily that even traces of ammonium acetate added to a refluxing solution of phenylindandione in glacial acetic acid produce a red coloration.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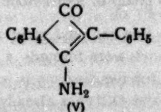
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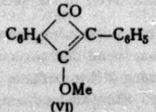
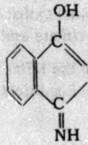

(VI)

The imine crystallizes beautifully, but is not very soluble in the usual organic solvents, especially in the cold. It dissolves in concentrated sulfuric acid giving a colorless solution; on dilution of the latter with water the red crystalline imine separates again. On heating with mineral acids the imine is hydrolyzed to phenylindandione. It is more stable toward alkalis.

In addition to the ketimino form (IV) phenylindandione imine might also be expected to exist in the enamine form (V). The problem of ketimine-enamine tautomerism of similar compounds has been repeatedly discussed in the literature [4, 5], but has so far not found an unequivocal solution. The enamine form would provide an excellent explanation for the intense color of the imine since it contains a conjugated double bond system identical with that present in the salts of phenylindandione (VI) which also have a red color. However, all attempts to confirm the presence of an amino group were unsuccessful. The compound does not give the usual reactions for primary amines, apart from a very weak carbylamine reaction; it does not form an acetyl derivative, does not condense with phthalic anhydride (a method by which it is possible to confirm almost any primary amino group) [6], and so on. From this it follows that the imine of phenylindandione exists in the ketimino form (IV). The intense color of the imine could be explained on the assumption of the existence of the enolic form (VII); however, the compound would then exhibit an acidic character, and this was not found to be the case. The color might also be explained as being due to the presence of a hydrogen bond as in the structure (VIII), but the color is exhibited also by the phenylimine or anil of phenylindandione (IX, R = $C_6H_5$) (although it is less intense), as well as by phenylindandione isobutylimine [XI, R= $CH_2CH(CH_3)_2$], and neither has a hydrogen atom attached to the nitrogen. The problem of the color of phenylindandione imine as well as of some other derivatives of phenylindandione, as for example, of its 2-amino-derivatives [7, 8] will have to be solved separately when the absorption spectra of these compounds have been investigated.



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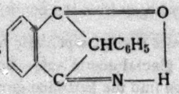

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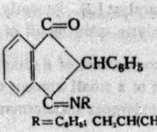
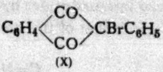


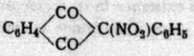
(IX)

The action of bromine on the imine (IV) gives 2-bromo-2-phenylindandione-1,3 (X) in almost quantitative yield. In an analogous manner, by the action of nitric acid, the imino group is easily split off with the formation of 2-nitro-2-phenylindandione-1,3 (XI).



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>CBrC_6H_5$$

(X)



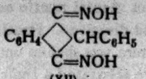
$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>C(NO_2)C_6H_5$$

(XI)

In order to establish how reactive the imino group is, we have investigated the possibility of condensing it with malonic acid or with its ester. There are indications in the literature [9] that Schiff's bases may react with malonic ester to give β-aminoacids. It may be that in the well-known synthesis of β-aminoacids (according to Rodionov) the reaction also proceeds through a stage involving the addition of malonic acid to the imine formed as an intermediate product [10]. However, all attempts to condense malonic ester with phenylindandione imine failed.

Imines also add on nitromethane under certain conditions [11]. Phenylindandione imine easily dissolves in nitromethane on heating and crystallizes again on cooling in the form of large red flakes. After prolonged refluxing of the solution, even in the presence of some pyridine or piperidine, the imine was always recovered unchanged. This shows that the reactivity of the ketimino group in β-diketones is not great.

Phenylindandione imine also contains a free carbonyl group and it was of interest to study its interaction with hydroxylamine. It was found that two compounds were formed: a mono- and a dioxime of phenylindandione. They could be separated using dichloroethane in which the dioxime is practically insoluble in the cold while the monoxime dissolves easily. Phenylindandione dioxime (XII) has already been described [12], whereas the monoxime (XIII) could not so far be prepared. When phenylindandione is reacted with an insufficient quantity of hydroxylamine only the dioxime is formed and some of the diketone remains unreacted. The formation of the monoxime was confirmed by hydrolysis of the compound to phenylindandione and hydroxylamine as well as by transforming it into the known dioxime. It is characteristic of both the monoxime and the dioxime that after drying at 100° their original melting points are changed, without the compounds having undergone a change in composition. This may be due to interconversion of the syn- and anti-forms of these oximes. Both the monoxime (XII) and the dioxime (XIII) dissolve in alkali; the dioxime gives a colorless solution and the monoxime a yellow one since it can also exist in the enolic form (XIV). The monoxime of 2-nitroindandione-1,3 undergoes the Beckmann transformation to give derivatives of isoquinoline [13]. Tentative experiments show that a similar transformation occurs also in the case of the monoxime of phenylindandione.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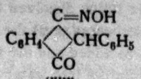
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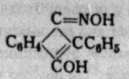
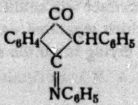

(XIV)

The action of aniline on phenylindandione imine leads to a slow exchange of the imino group by the phenylimino group to give the phenylamine (anil) of phenylindandione (XV) [14].

Reduction of phenylindandione imine in acid or alkaline medium always gave products which did not contain nitrogen.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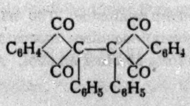
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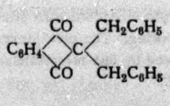
(XVII)

Phenylindandione easily undergoes oxidation as a result of which it loses its active hydrogen atom and forms a dimer — bisphenylindandione (XVI) [12]. All attempts to prepare an imine of this dimer failed: even after prolonged refluxing of the compound (XVI) with ammonium acetate in glacial acetic acid it could be recovered unchanged almost quantitatively. We also failed to prepare the imine of 2,2-dibenzylindandione-1,3 (XVII). From this it follows that in order to give an imine by interacting with ammonium acetate the diketone must contain an enolizable hydrogen atom; ammonium acetate will not react directly with a keto group. The mechanism of this reaction may therefore be pictured as follows: ammonium acetate reacts with the enolic form of the β-diketone giving the enamine (V). The latter is unstable and is immediately transformed into the ketamine (IV). The monoimine of the β-diketone does not enolize as easily; for example it does not dissolve in alkali. Consequently, the second keto group cannot form an imine under these conditions. Hence it also becomes clear why the β-diketone gives only the monoimine on reacting with ammonium acetate.

## EXPERIMENTAL

2-Phenylindandione-1,3 imine (IV). 5 g of phenylindandione was dissolved by heating in 50 ml of glacial acetic acid, 10 g of ammonium acetate was added and the mixture was refluxed for 20-25 minutes. The solution assumed a red color and became viscous. On cooling the contents of the flask solidified to a red crystalline mass. The solid which separated was filtered at the pump and washed with glacial acetic acid. Yield, 4.2 g (85%) of compound (IV), m.p. 260°. The substance was recrystallized from glacial acetic acid in the form of red plates.

Found %: N 6.25. $C_{15}H_{11}ON$. Calculated %: N 6.33.

The imine dissolves in pyridine in the cold and can be dissolved in glacial acetic acid and in nitrobenzene by heating; on cooling it crystallizes from these solvents in the form of red flakes; it is sparingly soluble in alcohol. It does not dissolve in dilute hydrochloric acid and does not change even on boiling with the dilute acid. It dissolves in concentrated hydrochloric acid, on heating, with red coloration which disappears on prolonged heating with the formation of a white precipitate of phenylindandione, m.p. 144°. Mixture of this precipitate with an authentic sample of phenylindandione melted without depression. Ammonia is evolved from the filtrate in the presence of excess alkali. The imine does not dissolve in alkalis even on boiling and no ammonia is evolved. On prolonged heating the solution assumes an orange color. On the other hand, alkaline reducing agents, for example, sodium and alcohol, or zinc dust and caustic soda, easily split off ammonia from the compound.

Bromination. 1 g of the imine was suspended in 10 ml of glacial acetic acid and a solution of 1 g of bromine in 5 ml of glacial acetic acid was added. Yield of 2-bromo-2-phenylindandione-1,3 (X) after recrystallization from alcohol, 1.3 g m.p. 104°. Mixture with a pure sample of the substance melted without depression.

Nitration. To a suspension of the imine in ether was added dropwise, with heating on a water-bath, concentrated nitric acid until the mixture assumed an orange color. On cooling there separated colorless crystals, m.p. 122°. Mixture with an authentic sample of 2-nitro-2-phenylindandione-1,3 melted without depression.

Found %: N 5.23. $C_{15}H_9O_4N$. Calculated %: N 5.24.

Oximination. To 10 g of phenylindandione imine dissolved in hot glacial acetic acid was added 6.5 g of hydroxylamine hydrochloride and the mixture was heated until the solid dissolved. Heating was discontinued and a further 3.5 g of hydroxylamine hydrochloride was added and the mixture was shaken until the orange solution no longer changed in appearance. On pouring the solution into water there separated a light pink to yellow precipitate. Yield, 10.1 g. The dried precipitate was shaken several times with dichloroethane (150 ml in all). Phenylindandione dioxime was filtered off. After two recrystallizations from alcohol and drying at 100° the substance melted at 223-224°. Mixture with a pure sample of the dioxime, prepared from phenylindandione and hydroxylamine hydrochloride [12] melted, after drying at 100°, without depression.

Found %: N 10.95. $C_{15}H_{12}O_2N_2$. Calculated %: N 11.11.

The filtrate was extracted with dilute sodium hydroxide. The orange extract was acidified with hydrochloric acid (1 : 1) with cooling. The precipitate of phenylindandione monoxime which separated was recrystallized from 50 % alcohol followed by one recrystallization from absolute alcohol. After drying in air the substance had a melting point of 116-117°.

Found %: N 5.78. $C_{15}H_{11}O_2N$. Calculated %: N 5.91.

Phenylindandione monoxime was dried at 100°. M. p. 152-153°.

Found %: N 5.58. $C_{15}H_{11}O_2N$. Calculated %: N 5.91.

Phenylindandione monoxime was heated with hydrochloric acid. The precipitate of phenylindandione melted at 145°. When mixed with a pure sample of phenylindandione it did not depress the melting point. The presence of hydroxylamine in the filtrate was confirmed by the Bamberger reaction [15].

A solution of the monoxime in pyridine was heated with hydroxylamine hydrochloride. The precipitate of phenylindandione dioxime was dried at 100° and had a melting point of 223-224° and did not depress the melting point when mixed with pure phenylindandione dioxime.

Found %: N 10.86. $C_{15}H_{12}O_2N_2$. Calculated %: N 11.11

2-Phenylindandione-1,3 phenylamine (anil) (XV). A mixture of 5 g of (IV), 4.2 g of aniline and 30 ml of glacial acetic acid was refluxed for 7 hours. After cooling the reaction mixture was filtered, the red crystals were boiled with a small amount of glacial acetic acid and the hot solution was filtered. Unreacted phenylindandione imine was retained on the filter while a mixture of the latter and phenylindandione phenylimine crystallized from the filtrate, m.p. 206-207°. Yield, 0.65 g. After two recrystallizations from alcohol the melting point was 222°. On heating with hydrochloric acid (1 : 1) the substance decomposed into phenylindandione and aniline.

Found %: N 4.80. $C_{21}H_{15}ON$. Calculated %: N 4.71.

Phenylindandione isobutylimine [IX, $R = CH_2CH(CH_3)_2$]. To a solution of 2 g of phenylindandione in 10 ml of glacial acetic acid was added 0.8 g of isobutylamine. The solution assumed a deep red color and on cooling the whole solidified to a crystalline mass. Yield, 1.4 g of orange-yellow crystals. After recrystallization from alcohol followed by recrystallization from benzene the substance melted at 132° and was found to be an adduct of phenylindandione isobutylimine and phenylindandione.

Found %: N 2.64. $C_{34}H_{29}O_3N$. Calculated %: N 2.80.

The substance obtained was boiled with sodium carbonate solution. Phenylindandione passed into solution as a red-colored salt, while phenylindandione isobutylimine formed a solid residue. After recrystallization from ethanol the orange crystals melted at 191°; at 180° the substance fused.

Found %: N 5.16. $C_{19}H_{19}ON$. Calculated %: N 5.05.

On heating with acids phenylindandione isobutylimine easily undergoes hydrolysis to phenylindandione and isobutylamine; it is stable toward alkalis. It can be brominated and nitrated more easily than phenylindandione imine.

To a solution of phenylindandione isobutylimine in glacial acetic acid was added a solution of bromine also in glacial acetic acid. The bromine solution was decolorized at once. After dilution with water and recrystallization from alcohol white crystals of 2-bromo-2-phenylindandione, m.p. 104°, were obtained. Mixture of the substance with an authentic sample melted without depression.

## SUMMARY

1. The imine of 2-phenylindandione-1,3 was prepared easily in the form of red crystals by the action of ammonium acetate in glacial acetic acid. The imine is stable toward alkalis and is slowly hydrolyzed by acids to phenylindandione and ammonia. The imino group can also be easily split off by bromination, nitration and reduction of the imine, with the formation of the corresponding derivatives of phenylindandione.

2. Treatment of phenylindandione imine with hydroxylamine gives a mixture of the monoxime and the dioxime of phenylindandione.

3. The ketimino linkage of phenylindandione imine does not exhibit any great reactivity.

## LITERATURE CITED

[1] A. A. Balandin and N. A. Vasyunina, Proc. Acad. Sci. USSR, 103, 831 (1955).

[2] M. A. Popov and N. I. Shuikin, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1951, 140.

[3] G. Vanag and E. Vanag, Bull. Acad. Sci. Latvian SSR, No. 9, (86), 137 (1954).

[4] C. Beyer, Ber. 24, 1662 (1891).

[5] K. v. Auwers and W. Susemihl, Ber, 63, 1072 (1930).

[6] G. Vanag, J. Gen. Chem. 17, 2080 (1947).

[7] G. Vanag and U. Walbe, Ber. 71, 1448 (1938).

[8] G. Ya. Vanag and A. K. Aren, J. Gen. Chem. 27, 1358 (1957).*

[9] K. Veigand, Experimental Methods of Organic Chemistry, Vol. II, p 665, (1952).**

[10] W. M. Rodionow and E. Th. Malewinskaja, Ber. 59, 2952 (1926).

[11] N. Leonhard, G. Leubner and E. Burk, J. Org. Chem. 15, 979 (1950).

[12] F. Nathanson, Ber. 26, 2576 (1893).

[13] G. Ya. Vanag and N. V. Vitol, J. Gen. Chem. 25, 1953 (1955).*

[14] G. Vanag and U. Walbe, Ber. 69, 1054 (1936).

[15] E. Bamberger, Ber. 32, 1805 (1899).

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* Original Russian pagination. See C. B. Translation.

** In Russian.

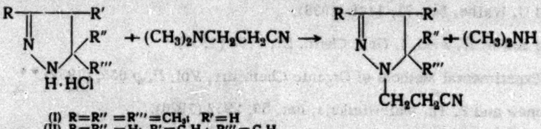
# REACTION OF HYDRAZINE DERIVATIVES

## XV. CYANOETHYLATION OF PYRAZOLINES

A. N. Kost, V. V. Ershov and S. I. Suminov

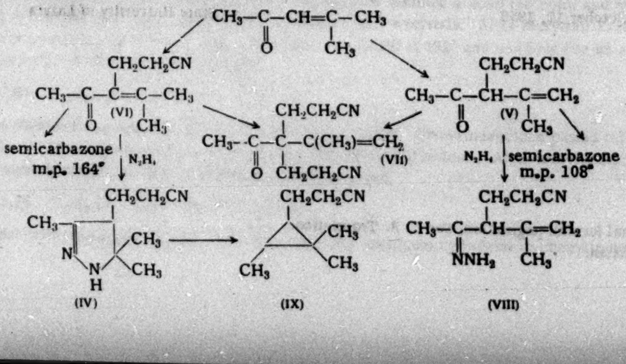
In one of our communications [1] we have pointed out that the interaction of acrylonitrile with pyrazolines proceeds anomalously: instead of the cyanoethylation reaction there takes place a vigorous polymerization of acrylonitrile initiated by free radicals formed as a result of the decomposition of pyrazolines. In order to effect the cyanoethylation of pyrazolines we have made use of the ability of β-dimethylaminopropionitrile to undergo transcyanoethylation reactions [2, 3] which take place under comparatively drastic conditions and pass, evidently, through the intermediate stage involving the splitting off of acrylonitrile. If, on the other hand, salts of the aminonitrile are used instead then the reaction proceeds with greater ease, as has been shown in the case of the interaction with aromatic amines, and the process takes place by an ionic mechanism [4].

It was found that no reaction took place on heating pyrazolines (having no substituent in position 1) with β-dimethylaminopropionitrile up to 200°. However, if an equivalent amount of hydrogen chloride is introduced into the reaction mixture (for example, if the hydrochloride of either the pyrazoline or of the aminonitrile is used) it is possible to obtain 1-(β-cyanoethyl)-pyrazolines at 170° in yields of 30-50 %.


R
R'
N
R''
N
R'''
H·HCl
+ (CH₃)₂NCH₂CH₂CN →
+ (CH₃)₂NH · HCl
CH₂CH₂CN

(I) $R=R''=R'''=CH_3$; $R'=H$
(II) $R=R''=H$; $R'=C_2H_5$; $R'''=C_3H_7$
(III) $R=R'''=C_6H_5$; $R'=H$; $R''=CH_3$

It was, of course, to be expected that under the influence of an acidic agent the cyanoethyl group would become attached to a carbon atom and not to the amino group. This type of change in the orientation is known in the case of indole (in alkaline solution cyanoethylation occurs at position 1, in acid solution — at position 3 [5]). On the other hand there are indications in the literature [6] that the hydrogen atom in position 4 (attached to a carbon atom) in pyrazolines can enter into substitution and condensation reactions. In view of this we have synthesized 3,5-trimethyl-4-(β-cyanoethyl)-pyrazoline (IV) in which the β-cyanoethyl group is in position 4. It was found that this substance differs markedly in its properties from the isomeric compound (I).


CH₃—C—CH=C—CH₃
O
CH₃
CH₂CH₂CN
CH₃—C—C=C—CH₃
O
(VI)
CH₃
semicarbazone
m.p. 164°
N₂H₄
CH₂CH₂CN
CH₃—C—C—C(CH₃)=CH₂
O
CH₂CH₂CN
(VII)
CH₂CH₂CN
CH₃—C—CH—C=CH₂
O
(V)
CH₃
N₂H₄
semicarbazone
m.p. 108°
CH₂CH₂CN
CH₃
N
N
H
CH₃
CH₃
CH₂CH₂CN
CH₃
CH₃
CH₃
CH₂CH₂CN
CH₃—C—CH—C=CH₂
NNH₂
CH₃

(IV) (IX) (VIII)

In order to prepare compound (IV) we have cyanoethylated mesityl oxide and obtained two mononitriles (V and VI) and one dinitrile (VII). The structure of the dinitrile (VII),the formation of which involves a shift of the double bond, was proved earlier [7]. As regards the nitriles (V) and (VI) which are the products of monocyanoethylation, these have been obtained previously only in very small quantities in admixture with each other and have not been characterized.

Our results show that when cyanoethylation is carried out with acrylonitrile (using sodium ethoxide as catalyst) in excess of mesityl oxide, the mixture of the two mononitriles (V and VI) is obtained in 57 % yield. These nitriles differ markedly in their physical constants and also give different semicarbazones. One of the nitriles had the structure of γ-acetyl-γ-isopropylidenebutyronitrile (VI), i.e. it contains a conjugated system as is confirmed by the fact that on interacting with hydrazine hydrate it is easily transformed into the pyrazoline (IV). The second nitrile has the structure of γ-acetyl-γ-isopropenylbutyronitrile (V) in which there is no conjugated system. On interacting with hydrazine hydrate it gives only the hydrazone (VIII) which easily splits off hydrazine (in the cold) under the action of hydrochloric acid or benzaldehyde. In contrast, the pyrazoline (IV) is not decomposed by hydrochloric acid and does not react with benzaldehyde. Under conditions of the Wolff-Kishner reaction it gave 1,1,3-trimethyl-2-(β-cyanoethyl)-cyclopropane (IX).

It might have been assumed that one of the ketonitriles (V or VI) would be a monocyanoethyl-derivative in which the cyanoethyl group would be attached to one of the methyl groups in mesityl oxide; however this is not the case since on further cyanoethylation both these nitriles give one and the same dinitrile (VII) of known structure.

## EXPERIMENTAL

1-(β-Cyanoethyl)-3,5,5-trimethylpyrazoline (I). A mixture of 20 g of 3,5,5-trimethylpyrazoline hydrochloride and 20 g of β-dimethylaminopropionitrile was refluxed at 170° for 1-1/4 hour with occasional shaking. After cooling the reaction mixture was made alkaline with 40 % sodium hydroxide, extracted with ether three times after which the ether was removed and the residue distilled in vacuo in a current of nitrogen. After two distillations there was obtained 10.3 g (47.9 %) of compound (I).

B.p. 115-116° (7 mm); $n_D^{20}$ 1.4718, $d_4^{20}$ 0.9698, $MR_D$ 47.73; calculated 47.62.

Found %: C 65.56, 65.59; H 9.27, 9.32. $C_9H_{15}N_3$. Calculated %: C 65.42; H 9.15.

When the reaction was carried out in p-xylene as solvent (refluxing for 5 hours) the yield dropped to 18 %. Shorter refluxing time reduces the yield still further. When the free bases were heated together at 200° for 5 hours no reaction occurred and the orginal compounds could be recovered quantitatively.

1-(β-Cyanoethyl)-4-ethyl-5-propylpyrazoline (II) was obtained from 40 g of 4-ethyl-5-propylpyrazoline hydrochloride [8] and 40 g of β-dimethylaminopropionitrile in a manner similar to the one described in the foregoing preparation. Yield, 21.6 g (46 %).

B. p. 129° (6 mm), $n_D^{20}$ 1.4739, $d_4^{20}$ 0.9509, $MR_D$ 56.98; calculated 56.86.

Found %: C 68.34, 68.60; H 10.07, 10.19. $C_{11}H_{19}N_3$. Calculated %: C 68.35; H 9.91.

1-(β-Cyanoethyl)-5-methyl-3,5-diethylpyrazoline (III). This compound was obtained in a similar manner from 34 g of 5-methyl-3,5-diethylpyrazoline hydrochloride [9] and 40 g of β-dimethylaminopropionitrile by refluxing the mixture for one hour with good stirring. Yield, 10.2 g (28 %).

B. p. 122-123.5° (5 mm), $n_D^{20}$ 1.4773, $d_4^{20}$ 0.9615, $MR_D$ 56.83; calculated 56.86.

Found %: C 68.40, 68.27; H 10.08, 10.16. $C_{11}H_{19}N_3$. Calculated %: C 68.35; H 9.91.

Cyanoethylation of mesityl oxide. Mesityl oxide was washed with 2 N sodium carbonate, and water, and was dried and distilled. To 392 g of freshly prepared mesityl oxide was added sodium ethoxide (0.5 g of metallic sodium in 10 ml of anhydrous alcohol). The mixture was then cooled in ice and 53 g of acrylonitrile was introduced dropwise, with vigorous stirring, at such a rate as to keep the temperature of the reaction mixture below 8-10°. When all the acrylonitrile was added stirring was continued for 1/2 hour with cooling, followed by stirring for 2 hours at room temperature. The mixture was then acidified with 2 N hydrochloric acid, washed carefully with water until neutral, dried and distilled in vacuo.

After fractional distillation there was obtained 34.7 g (23 %) of compound (V).

B. p. 79-80° (1 mm), $n_D^{20}$ 1.4592, $d_4^{20}$ 0.9572, $MR_D$ 43.20; calculated 43.12.

The semicarbazone melts at 108° (from aqueous alcohol).

Found %: C 57.77, 57.86; H 7.48, 7.56. $C_{10}H_{16}ON_4$. Calculated %: C 57.67; H 7.74.

In addition to compound (V) there was obtained 51.3 g (34 %) of γ-acetyl-γ-isopropylidenebutyronitrile (VI).

B. p. 88.5-90° (1.5 mm), $n_D^{20}$ 1.4780, $d_4^{20}$ 0.9825, $MR_D$ 43.56; calculated 43.12; $EM_D$ 0.44.

Found %: C 71.60, 71.69; H 8.81, 8.93. $C_9H_{13}ON$. Calculated %: C 71.48; H 8.66.

The semicarbazone melts at 164° (from aqueous alcohol).

Found %: C 57.83, 57.94; H 7.40, 7.51. $C_{10}H_{16}ON_4$. Calculated %: C 57.67; H 7.74.

When the reaction was carried out using a larger excess of mesityl oxide there was no increase in the yield of monocyanoethyl-derivatives while with reduced proportions of the reactants there formed considerable amounts of dicyanoethyl-derivatives with a simultaneous reduction in the yields of the ketonitriles (V) and (VI).

**γ-Acetyl-γ-isopropenylpimelonitrile (VII).** To 5 g of the ketonitrile (V) was added 3 g of acrylonitrile in the presence of sodium ethoxide. The reaction took place with evolution of heat. The crystals which separated were recrystallized from methanol. Yield, 4.7 g (71%), m.p. 116° [7]. Under the same conditions the ketonitrile (VI) also forms compound (VII). No melting point depression could be observed for the mixture of the ketonitriles (VII) obtained in each case.

**3,5,5-Trimethyl-4-(β-cyanoethyl)-pyrazoline (IV).** To a solution of 15 g of hydrazine hydrate in 20 ml of alcohol was added gradually 35.7 g of the ketonitrile (VI). The mixture was refluxed for 1-1/2 hours and was then distilled in vacuo in a current of nitrogen. Yield, 28 g (66 %).

B. p. 132-134° (4 mm), $n_D^{20}$ 1.4920, $d_4^{20}$ 1.0201, $MR_D$ 46.99; calculated 47.25.

The pyrazoline is very unstable. It does not react with benzaldehyde. In anhydrous benzene solution it reacts with methyl iodide to give the methiodide, m.p. 182° (from absolute alcohol).

Found %: C 38.88, 38.96; H 6.07, 6.09; N 13.88, 13.96. $C_{10}H_{18}N_3I$. Calculated %: C 39.09; H 5.90; N 13.72.

Under similar conditions the ketonitrile (V) forms the hydrazone (VIII).

B. p. 126° (3 mm), $n_D^{20}$ 1.4978, $d_4^{20}$ 0.9867, $MR_D$ 49.18; calculated 49.06.

The hydrazone (VIII) reacts with benzaldehyde with strong evolution of heat to give benzalazine in almost quantitative yield, the latter having an m.p. of 93°.

**1,1,3-Trimethyl-2-(β-cyanoethyl)-cyclopropane (IX).** 21 g of freshly prepared pyrazoline (IV) was heated with finely divided platinum and caustic potash containing a trace of silver. The reaction occurred with vigorous evolution of nitrogen. The contents of the flask were distilled collecting the fraction up to 220° which was subsequently fractionated in vacuo. Yield of compound (IX), 7.3 g (40%).

B. p. 67-68.5° (7 mm), $n_D^{20}$ 1.4814, $d_4^{20}$ 0.9281, $MR_D$ 42.11; calculated 42.08.

Found %: N 10.39, 10.50. $C_9H_{15}N$. Calculated %: N 10.22.

## SUMMARY

1. It has been found that pyrazolines may be cyanoethylated in position 1 provided β-dimethylaminopropionitrile, instead of acrylonitrile, is used with some hydrogen chloride.

2. A pyrazoline containing the β-cyanoethyl group in position 4 has been prepared. The structure of monocyanoethyl-derivatives of mesityl oxide has been established.

## LITERATURE CITED

[1] A. N. Kost and V. V. Ershov, Bull. Moscow State Univ. No. 12, 115 (1955).

[2] A. P. Terentyev, A. N. Kost and S. M. Gurvich, J. Gen. Chem. 23, 615 (1953).*

[3] A. N. Kost and V. V. Ershov, J. Gen. Chem. 26, 3132 (1956).*

[4] J. Cymerman-Craig, M. Moyle, A. Nicholson and R. Werner, J. Chem. Soc. 1955, 3698.

[5] A. P. Terentyev, A. N. Kost and V. A. Smit, J. Gen. Chem. 25, 1959 (1955);* 26, 557 (1956).*

[6] T. Curtius and E. Wirsing, J. pr. Chem. [2], 50, 548 (1894).

[7] H. Bruson and T. Reiner, J. Am. Chem. Soc. 65, 18 (1943).

[8] A. N. Kost and I. I. Grandberg, J. Gen. Chem. 26, 2319 (1956).*

[9] A. N. Kost and I. I. Grandberg, J. Gen. Chem. 26, 1717 (1956).*

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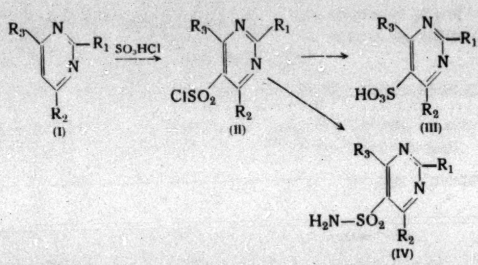
# SYNTHESES AND TRANSFORMATIONS OF PYRIMIDINE DERIVATIVES

## IX. SULFO-DERIVATIVES OF CYTOSINE, 4-METHYLCYTOSINE AND URACIL

N. V. Khromov-Borisov and R. S. Karlinskaya

Among 5-sulfo-derivatives of pyrimidine which we have recently described [1], some have been found to exhibit a cytostatic action on blood as demonstrated in experiments with animals [2]; this renders the compounds interesting as possible therapeutic agents in leukemia — a serious disease of the blood. In our communication (V) it was shown [1] that the action of chlorosulfonic acid on pyrimidine derivatives having two electron-donor substituents in positions 2, 4, and to a lesser degree those having these substituents in position 6, provides an excellent method of preparation of the corresponding pyrimidine-5-sulfonic acids (III).



It was also found that in the majority of cases it was impossible to establish the formation of chlorosulfonates (II) as intermediate products of the reaction. Only in one case (I, $R_1 = R_3 = NH_2$; $R_2 = CH_3$) was a chlorosulfonate obtained (II, $R_1 = R_3 = NH_2$; $R_2 = CH_3$), which hydrolyzed in aqueous acid solution to give the corresponding sulfonic acid (III, $R_1 = R_3 = NH_2$; $R_2 = CH_3$).

In the present work we investigated the interaction of chlorosulfonic acid with cytosine (I, $R_1 = OH$; $R_2 = H$, $R_3 = NH_2$), 4-methylcytosine (I, $R_1 = OH$; $R_2 = CH_3$; $R_3 = NH_2$) and uracil($R_1 = R_3 = OH$; $R_2 = H$). In the case of the first two compounds the corresponding sulfonic acids (III) were obtained with ease. The reaction took place at 100-110° and no chlorosulfonates (II) could be detected as intermediate products. The resulting sulfonic acids are white crystalline substances which dissolve easily in strong alkalis as well as in alkaline carbonates, but are difficultly soluble in water. We have also prepared the sodium salts of these acids. The salts are easily soluble in water and possess the characteristic property of efflorescing on being heated on a metallic foil.

In the case of the interaction of chlorosulfonic acid with uracil the reaction takes a different course. The optimum reaction temperature in this case is 100-110°. However, the final product is not the sulfonic acid (III), but its chloride (II, $R_1 = R_3 = OH$; $R_2 = H$). This compound has been obtained previously as an intermediate product in the synthesis of 5,5'-uracil-disulfide [3], but was not characterized at that time. In addition, the author of the paper cited stated erroneously that chlorosulfonation of uracil should not be carried out at temperatures above 40°. The chloride of 2,6-dihydroxypyrimidine-5-sulfonic acid can be isolated after chlorosulfonation only when the cooled reaction mixture is poured into a definite amount of ice (see Experimental) and the precipitate which forms is immediately separated from the acid solution. The substance is obtained in the form of a fine white powder (when moist the substance exhibits a characteristic glitter similar to that of mother-of-pearl) and is found to be very reactive. It does not change on being heated up to 260°, but decomposes at 260-270°. It is markedly soluble in cold water, and slightly soluble in alcohol and acetone. On interacting with alcoholic ammonia in the cold it is transformed into 2,6-dihydroxypyrimidine-5-sulfonamide (IV, $R_1 = R_3 = OH$; $R_2 = H$). In aqueous sodium carbonate, in the cold, or on being heated in acetic acid in the presence of sodium acetate, it forms the sodium salt of 2,6-dihydroxypyrimidine-5-sulfonic acid which, after recrystallization from water, is obtained as a crystalline substance containing one molecule of water of crystallization. On being heated on a metal foil the salt effloresces. Its aqueous solution is neutral.

In the presence of mineral acids 2,6-dihydroxypyrimidine-5-chlorosulfonate is very easily transformed into uracil. Thus, for example, if the reaction mixture is poured on ice and the resultant solution is then allowed to stand for some time, the chlorosulfonate is completely transformed into uracil. When attempts were made to recrystallize the chlorosulfonate from water the substance again changed into uracil. In this respect the chlorosulfonate differs from 2,6-diamino-4-methylpyrimidine-5-chlorosulfonate which under analogous conditions does not change into 2,6-diamino-4-methylpyrimidine, but into the corresponding sulfonic acid.

Uracil-5-sulfonic acid is considerably more stable in mineral acid solutions than is uracil-5-chlorosulfonate. When sodium uracil-5-sulfonate is heated with 10% aqueous hydrochloric acid traces of $SO_4''$ ions appear only after 2 hours.

## EXPERIMENTAL

*2-Hydroxy-6-amino-4-methyl-5-sulfopyrimidine.* 2.0 g of 2-hydroxy-6-amino-4-methylpyrimidine[4] was added gradually to 8 ml of chlorosulfonic acid which had been heated to 110°. The temperature of the reaction mixture was kept between 110 and 120°. 10 minutes after the end of the reaction the mixture was poured into 40 g of ice with good external cooling. The next day the greyish-white precipitate was filtered off and washed with water. Yield, 2.0 g (60 %). After recrystallization from water the substance melted at 290-291°.

Found %: S 16.1, 16.0; N 20.2, 20.4. $C_5H_7O_4N_3S$. Calculated %: S 15.6; N 20.4.

On addition of excess sodium acetate to the solution obtained after the reaction mixture was poured on ice, the sulfonic acid separated in the form of its sodium salt which is more soluble in water than the free acid. M. p. 273°.

*2-Hydroxy-6-amino-5-sulfopyrimidine.* 2.0 g of cytosine [5] was added in portions, with stirring, to 10 ml of chlorosulfonic acid heated to 110°. The reaction mixture was then poured into 30 g of ice with good external cooling. The white crystalline percipitate was filtered off and washed with water. Yield, 1.5 g (44 %). The substance was recrystallized from water.

Found %: N 21.9, 21.8. $C_4H_5O_4N_3S$. Calculated %: N 21.9.

1.95 g of 5-sulfocytosine was treated with a solution of 0.2 g of sodium hydroxide in 10 ml of water and the mixture was evaporated to dryness. The residue was recrystallized from water with charcoal.

Found %: Na 10.5; S 14.9. $C_4H_4O_4N_3SNa$. Calculated %: Na 10.7; S 15.0.

*The action of chlorosulfonic acid on uracil.* *a) Preparation of uracil-5-chlorosulfonate.* 6 g of uracil [6] was added gradually with stirring to chlorosulfonic acid (24 ml) which had been heated to 100-110°. The mixture was then poured into 180 g of ice, with external cooling. The white precipitate of the chlorosulfonate which separated was filtered off after 10 minutes, washed once with ice-water, treated several times with cooled alcohol (until the filtrate was free of $SO_4$ ions) and finally washed with ether. The substance was dried in air or in a desiccator. Yield, 3.0 g (25 %).

Found %: Cl 15.8, 15.8. $C_4H_3O_4N_2ClS \cdot H_2O$. Calculated %: Cl 15.6.

If the precipitate of uracil-5-chlorosulfonate is left in the acid solution (after pouring the reaction mixture into ice) for several hours, the compound undergoes transformation into uracil.

*b) Transformation of uracil-5-chlorosulfonate into uracil.* When attempts were made to recrystallize uracil-5-chlorosulfonate from water the substance changed into a white crystalline material which contained no chlorine or sulfur. It was identified as uracil.

Found %: N 24.8, 24.9. $C_4H_4O_2N_2$. Calculated %: N 25.0.

c) Preparation of uracil-5-sulfonamide. 2 g of uracil was sulfonated with chlorosulfonic acid (see above), the chlorosulfonate which formed was filtered off, washed once with ice-water, once with alcohol and was at once treated with excess of saturated alcoholic ammonia solution (10 ml) at room temperature. After three hours the white crystalline precipitate of the sulfonamide was filtered off and washed with alcohol. Yield, 1.0 g (30 %). The substance is soluble in water and can be recrystallized from it. It is insoluble in alcohol and does not change on heating to 300°.

Found %: N 21.6, 21.7; S 17.0, 16.9. $C_4H_5O_4N_3S$. Calculated %: N 21.9; S 16.9.

d) Preparation of sodium uracil-5-sulfonate.

1) Uracil-5-chlorosulfonate (3.0 g) was dissolved in 30 ml of a 10 % sodium carbonate solution (with effervescence and foaming). The solution was evaporated to dryness and the residue recrystallized from water with charcoal. Yield of the sodium salt, 2.2 g (73 %, calculated on the chlorosulfonate).

2) Uracil-5-chlorosulfonate, obtained from 4 g of uracil, was washed once with water and twice with alcohol and dissolved in a minimum amount of water. To this solution was added excess of sodium acetate and 5 ml of glacial acetic acid. The solution was heated on a water bath for 45 minutes and was then evaporated to dryness. The residue was recrystallized from water with charcoal. Yield of the sodium salt, 1.0 g (17 %, calculated on the uracil).

Found %: $H_2O$ 7.3; N 12.4, 12.0; S 14.0, 13.9, 14.1; Na 10.0, 9.9. $C_4H_3O_5N_2SNa \cdot H_2O$. Calculated %: $H_2O$ 7.7; N 12.2; S 13.9; Na 9.9.

The action of hydrochloric acid on sodium uracil-5-sulfonate. The salt was heated with 10 % aqueous hydrochloric acid to which had been added some 2 % barium acetate solution. After 2 hours heating the solution became turbid (precipitation of barium sulfate).

## SUMMARY

1. The action of chlorosulfonic acid on cytosine and on 4-methylcytosine gives, respectively, 2-hydroxy-6-aminopyrimidine-5- and 2-hydroxy-6-amino-4-methylpyrimidine-5-sulfonic acids. The sodium salts of both sulfonic acids have also been prepared.

2. It has been shown that the interaction of uracil with chlorosulfonic acid results in the formation of uracil-5-chlorosulfonate as the primary product.

3. When acted upon by ammonia, uracil-5-chlorosulfonate is transformed into uracil-5-sulfonamide.

4. Treatment of uracil-5-chlorosulfonate with sodium carbonate or sodium acetate solution gives the sodium salt of uracil-5-sulfonic acid.

5. Under the action of aqueous mineral acids uracil-5-chlorosulfonate is transformed into uracil.

6. Uracil-5-sulfonic acid is fairly stable in acid solutions, in contrast to uracil-5-chlorosulfonate.

## LITERATURE CITED

[1] N. V. Khromov-Borisov and R. S. Karlinskaya, J. Gen. Chem. 24, 2212 (1954).*

[2] N. V. Lazarev, R. S. Karlinskaya and G. I. Felistovich, Problems of Oncology, No. 2, 216 (1956).

[3] G. R. Barker, J. Chem. Soc. 1954, 4206.

[4] Johns, Am. Chem. J. 40, 352 (1908).

[5] R. S. Karlinskaya and N. V. Khromov-Borisov, J. Gen. Chem. 27, 2113 (1957).*

[6] Davidson and Baudisch, J. Am. Chem. Soc. 48, 2379 (1926).

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# REACTION PRODUCTS OF EPICHLOROHYDRIN WITH AROMATIC AMINES

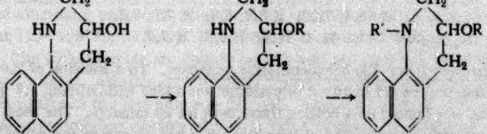
## II. 1, 2, 3, 4-TETRAHYDRO-3-HYDROXY-7,8-BENZOQUINOLINE

N. N. Vorozhtsov, Jr. and S. I. Kutkevichus

The reactions of the 1, 2, 3, 4-tetrahydro-3-hydroxy derivatives of quinoline, the same as of the 3-hydroxy derivatives of piperidine, have been studied but slightly up to now. We investigated some of the reactions of this group of compounds using the comparatively available 1, 2, 3, 4-tetrahydro-3-hydroxy-7,8-benzoquinoline (I).

Benzoylation of (I) with an equimolar amount of benzoyl chloride in pyridine yields the O-benzoyl derivative (II, R = $C_6H_5CO$). The structure of this compound is shown by the fact that it retains the basic properties of the original hydroxy amine and forms a crystalline hydrochloride. The treatment of (I) with excess benzoyl chloride (also in pyridine) gave the O, N-dibenzoyl derivative (III, R = R' = $C_6H_5CO$), which is lacking in basic properties.

The benzylation of (I) with benzyl chloride in the presence of sodium hydroxide yields the O-benzyl ether (II, R = $C_6H_5CH_2$). Its structure was shown by the fact that the benzoyl derivative obtained from it does not possess basic properties and, consequently, can be only 1, 2, 3, 4-tetrahydro-3-benzyloxy-N-benzoyl-7, 8-benzoquinoline (III, R = $C_6H_5CH_2$, R' = $C_6H_5CO$).



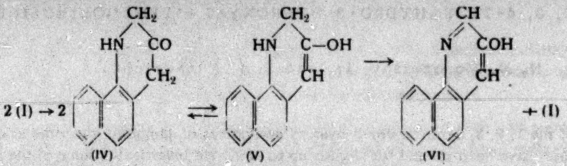
(I) (II) (III)

The predominant reactivity of the hydroxyl group in (I) is in agreement with the data, obtained by P. P. Shorygin and V. N. Belov in studying the reactions of the hydroxyethyl derivatives of aniline [1] and, possibly, is due to the low basicity of the secondary amino group, linked to the aromatic ring, and also possibly, due to the sterically hindered nitrogen atom.

To obtain the corresponding keto compound — 1, 2, 3, 4-tetrahydro-3-oxo-7,8-benzoquinoline — from (I) we oxidized (I) by the Oppenauer technique [2]. It is indicated in the literature that whereas the 1,2-amino alcohols are frequently not amenable to Oppenauer oxidation, the 1,2-anilino alcohols are oxidized by this method to the corresponding keto compounds [3]. The oxidation went quite smoothly when (I) was heated with aluminum phenolate and excess cyclohexanone in toluene. However, the oxidation product (m.p. 209.1 — 209.5°) did not show the properties of a ketone. For a ketone having the structure of (IV) the solubility in alkali is also not understood, nor is the ability of the benzoyl derivative to form a hydrochloride. The reactions and analysis of the product obtained by us correspond to 3-hydroxy-7,8-benzoquinoline (VI), only the melting point is somewhat higher than that given in the literature (201 - 203°) [4]. However, the 3-hydroxy-7,8-benzoquinoline obtained by us using the method described in the literature (dehydrogenation of (I) with phenol in the presence of Raney-Ni), after recrystallization from $CH_3OH$, melted at practically the same temperature (208.5 - 209°)

as the product obtained by the Oppenauer method. The identity of the product obtained by Oppenauer oxidation with 3-hydroxy-7,8-benzoquinoline was shown by the fact that the mixed melting point was not depressed.

The somewhat unexpected cleavage of 4 hydrogen atoms in the oxidation of the alcohol by the Oppenauer method (to the best of our knowledge not reported before) is evidently explained by the fact that the initially formed ketone (IV) is tautomeric with 1,2-dihydro-3-hydroxy-7,8-benzoquinoline (V), or with the corresponding 1,4-dihydro derivative. The dihydro derivative of the quinoline then undergoes disproportionation to yield the corresponding quinoline and its tetrahydro derivative – in our case 3-hydroxy-7,8-benzoquinoline and the starting alcohol (I) (which then undergoes further oxidation).



## EXPERIMENTAL

**1, 2, 3, 4-Tetrahydro-3-hydroxy-7,8-benzoquinoline (I).** The preparation of (I) by the cyclization of N-(γ-chloro-β-hydroxypropyl)-1-naphthylamine was described earlie [5]. (I) can be obtained more simply by the direct reaction of epichlorohydrin with 1-naphthylamine [4]. A mixture of 14.3 g of 1-naphthylamine, 9.3 g of epichlorohydrin and 12.5 ml of chlorobenzene was heated at 135 - 145° for 8 hours. After cooling to 30 - 40° the (I) hydrochloride was filtered and washed with chlorobenzene. Yield 11.4 g (48.2%). M.p. 245°. The yield of the hydrochloride can be raised somewhat (up to 58.6%) if before adding the chlorobenzene and heating the mixture of 1-naphthylamine and epichlorohydrin is kept at room temperature for a long time (14 days).

The free base (I) is conveniently obtained from the hydrochloride by dissolving the latter in 1.25 parts of pyridine at 70 - 80°, followed by dilution of the hot solution with 2 parts of water. Recrystallization from chlorobenzene gave colorless needles with m.p. 151.9 - 152.2°. The literature gives m.p. 152° [4].

Found %: C 78.4, 78.2; H 6.7, 6.6; N 7.1, 7.2.
$C_{13}H_{13}ON$. Calc. %: C 78.4; H 6.6; N 7.0.

**1, 2, 3, 4-Tetrahydro-3-hydroxy-7,8-benzoquinoline Benzoate.** To a solution of 2.0 g of 1, 2, 3, 4-tetrahydro-3-hydroxy-7,8-benzoquinoline (I) in 10 ml of pyridine was added with stirring 1.7 g of benzoyl chloride in drops. The reaction mass was heated on a boiling water bath for 30 minutes. The mass after cooling was diluted with 250 ml of water with stirring. The viscous product, after decanting the upper water layer and washing with water, was dried and treated with 8 ml of methyl alcohol. The insoluble 1, 2, 3, 4-tetrahydro-3-hydroxy-7, 8-benzoquinoline (0.32 g) was filtered. The residue, obtained after evaporating the methyl alcohol from the filtrate in a desiccator, was recrystallized from methyl alcohol; colorless plates, m.p. 124.7 - 125°.

Found %: C 79.0, 79.0; H 5.7, 5.8; N 4.8, 4.8.
$C_{20}H_{17}O_2N$. Calc. %: C 79.2; H 5.7; N 4.6.

**1, 2, 3, 4-Tetrahydro-3-hydroxy-7,8-benzoquinoline Benzoate Hydrochloride.** A solution of 0.6 g of 1, 2, 3, 4-tetrahydro-3-hydroxy-7,8-benzoquinoline benzoate in 50 ml of ether was saturated with hydrogen chloride. The hydrochloride precipitate was recrystallized from methyl alcohol; colorless plates with a luster, m.p. 172.7 - 173.6°.

Found %: C 70.9, 70.8; H 5.5, 5.4; $Cl^-$ 10.3, 10.3.
$C_{20}H_{17}O_2N \cdot HCl$. Calc. %: C 70.7; H 5.3; $Cl^-$ 10.4.

**1, 2, 3, 4-Tetrahydro-N-benzoyl-3-hydroxy-7,8-benzoquinoline Benzoate.** A solution of 2.0 g of (I) in 6.0 ml of pyridine was treated with stirring with 4.3 g of benzoyl chloride. The reaction mass was heated on a boiling water bath for 1.75 hours. The mass after cooling was slowly diluted with stirring with 20 ml of 25% sulfuric acid solution, and then with 40 ml of water. After decanting the top water layer the viscous oil obtained here was washed with water, dried, and treated with 25 ml of methyl alcohol. The crystalline precipitate was filtered and washed with 6 ml of methyl alcohol. Weight 3.2 g, m.p. 143.0 - 144.6°. Recrystallization from alcohol gave colorless needles, m.p. 148.7 - 149.5°.

Found %: C 79.4, 79.4; H 5.3, 5.4; N 3.8, 3.8.
$C_{27}H_{21}O_3N$. Calc. %: C 79.6; H 5.2; N 3.4.

The same product was also obtained by running the reaction for 5 days at room temperature.

1, 2, 3, 4-Tetrahydro-3-benzyloxy-7,8-benzoquinoline Hydrochloride. A mixture of 2.0 g of (I), 2.8 g of benzyl chloride, 5 ml of cyclohexanone and 0.88 g of sodium hydroxide was heated on a boiling water bath for 28 hours. The reaction mass was dissolved in 75 ml of ether and washed with water until the test for both chloride and hydroxyl ions was negative. After distilling off the ether, the water and cyclohexanone were vacuum-distilled on a boiling water bath. The residue, a transparent, nearly immobile mass at room temperature, was dissolved in 15 ml of methyl alcohol and the solution saturated with hydrogen chloride. The 1, 2, 3, 4-tetrahydro-3-benzyloxy-7,8-benzoquinoline hydrochloride precipitate was filtered and washed with 3 ml of methyl alcohol. Weight 1.3 g, m.p. 177° (decompn.). Recrystallization from methyl alcohol gave colorless crystals with m.p. 180.4° (decompn.).

Found %: C 73.6, 73.6; H 6.3, 6.4; N 4.7, 4.5; $Cl^-$ 10.8, 10.8.
$C_{20}H_{19}ON \cdot HCl$. Calc. %: C 73.7; H 6.2; N 4.3; $Cl^-$ 10.9.

1, 2, 3, 4-Tetrahydro-N-benzoyl-3-benzyloxy-7,8-benzoquinoline. A mixture of 0.3 g of 1, 2, 3, 4-tetrahydro-3-benzyloxy-7,8-benzoquinoline hydrochloride with m.p. 180.4°, 3 ml of pyridine and 0.55 g of benzoyl chloride was heated on a boiling water bath for 5 hours. The reaction mass was diluted with 15 ml of 25% sulfuric acid, and then with 50 ml of water. The viscous mass that remained after decanting the top water layer was washed several times with water and dried. Several recrystallizations from methyl alcohol gave white needles of 1, 2, 3, 4-tetrahydro-N-benzoyl-3-benzyloxy-7,8-benzoquinoline with m.p. 104.6 - 105.0°.

Found %: C 82.2, 82.3; H 6.0, 5.8.
$C_{27}H_{23}O_2N$. Calc. %: C 82.4; H 5.9.

Saturation of an alcohol solution of the compound with hydrogen chloride failed to give the hydrochloride.

Oxidation of 1,2,3,4-Tetrahydro-3-hydroxy-7,8-benzoquinoline by the Oppenauer Method. A mixture of 10.5 g (I), 27.5 g of aluminum phenolate, 200 ml of dry cyclohexanone and 1300 ml of dry toluene was heated in a paraffin bath at 115 - 125° for 20 hours. The reaction mass was filtered, and the filtrate was saturated with hydrogen chloride. The hydrochloride precipitate was filtered and dissolved in 50 ml of methyl alcohol. The filtered solution was made alkaline with 5% $NaHCO_3$ solution, and then it was diluted with water to a volume of 250 ml. The precipitate of the free base was filtered. Weight 4.1 g, m.p. 202.0 - 203.6°. Recrystallization from methyl alcohol gave colorless needles with m.p. 209.1 - 209.5°. The substance is soluble in alcohol, acetone, dilute sodium hydroxide solution, and also in dilute hydrochloric acid.

We were unable to obtain either the phenylhydrazone or the oxime from the substance with m.p. 209.1 - 209.5°. The analysis data correspond to those calculated for 3-hydroxy-7,8-benzoquinoline.

Found %: C 79.8, 79.9; H 4.8, 4.7.
$C_{13}H_9ON$. Calc. %: C 80.0; H 4.7.

3-Hydroxy-7,8-benzoquinoline Hydrochloride. A solution of 0.7 g of 3-hydroxy-7,8-benzoquinoline in 10 ml of methyl alcohol and 1 ml of water was saturated with HCl. The 3-hydroxy-7,8-benzoquinoline hydrochloride precipitate was filtered and washed with methyl alcohol. Weight 0.75 g, m.p. 264° (decompn.).

Recrystallization from alcohol gave colorless needles with a luster, m.p. 265.5° (decompn.). The substance has 1 mole of crystallization water.

Loss in weight after 10 days over $CaCl_2$, in %: 7.0, 7.1.
$C_{13}H_{10}NOCl \cdot H_2O$. Calc. %: $H_2O$ 7.2.

The needles partially decompose during drying and lose their luster. The anhydrous substance was analyzed.

Found %: C 67.2, 67.3; H 4.5, 4.4; $Cl^-$ 15.3.
$C_{13}H_9ON \cdot HCl$. Calc. %: C 67.4; H 4.4; $Cl^-$ 15.3.

3-Hydroxy-7,8-benzoquinoline Picrate. The picrate obtained from 0.10 g of 3-hydroxy-7,8-benzoquinoline and 0.12 g of picric acid in alcohol (6 ml) was filtered and washed with alcohol. Weight 0.18 g. m.p. 238.1 - 239.1°. Recrystallization from methyl alcohol gave yellow needles with m.p. 241.8 - 242.3°.

Found %: N 13.4, 13.3.
$C_{19}H_{12}O_8N_4$. Calc. %: N 13.2.

3-Hydroxy-7,8-benzoquinoline Benzoate. A mixture of 0.6 g of 3-hydroxy-7,8-benzoquinoline, 2 ml of pyridine and 1.8 g of benzoyl chloride was heated on a boiling water bath for 4 hours. The mass after cooling was diluted with 8 ml of 25% sulfuric acid, and then with 25 ml of water. The precipitate was filtered and washed with methyl alcohol. Weight 0.63 g, m.p. 121.1 - 121.6°. Recrystallization from methyl alcohol gave colorless needles with m.p. 123.1 - 123.3°.

Found %: C 80.4, 80.3; H 4.6, 4.5.
$C_{20}H_{13}O_2N$. Calc. %: C 80.3; H 4.4.

3-Hydroxy-7,8-benzoquinoline Benzoate Hydrochloride. A solution of 0.4 g of 3-hydroxy-7,8-benzoquinoline benzoate in 10 ml of methyl alcohol was saturated with HCl. The precipitate was cooled to -3 to -5° and filtered, washed with methyl alcohol, and dried over sodium hydroxide; colorless needles, weight 0.35 g, m.p. 178° (decompn.). The substance contains chlorine ion.

Counter Synthesis of 3-Hydroxy-7,8-benzoquinoline. A mixture of 2.0 g of (I), 0.9 g of Raney-Ni (washed with methyl alcohol) and 7.8 g of phenol was heated in an oil bath (200 - 210°) for 8 hours. The reaction mass was first treated with 70 ml of 25% sodium hydroxide solution and then diluted with 100 ml of water. The insoluble residue solidified in 12 hours. The filtrate was treated with 10% hydrochloric acid until acid. The precipitate of the hydrochloride was filtered and washed with water. Weight 0.5 g. Recrystallization from methyl alcohol gave 3-hydroxy-7, 8-benzoquinoline hydrochloride as needles with m.p. 265° (decompn.).

Found %: $Cl^-$ 15.0, 15.1.
$C_{13}H_9ON \cdot HCl$. Calc. %: $Cl^-$ 15.3.

A solution of 0.3 g of 3-hydroxy-7,8-benzoquinoline hydrochloride in 50 ml of water, obtained by heating, was treated with 5% $NaHCO_3$ solution. The precipitate of the free base was filtered and washed with water, weight 0.2 g, m.p. 200.0 - 202.5°. After recrystallization from methyl alcohol, m.p. 208.5 - 209.0°.

Found %: C 79.9, 80.1; H 4.7, 4.8.
$C_{13}H_9ON$. Calc. %: C 80.0; H 4.7.

The mixed melting point of the compound with the 3-hydroxy-7,8-benzoquinoline (m.p. 209.1 - 209.5°) obtained by Oppenauer oxidation was not depressed.

## SUMMARY

1. The benzoylation and benzylation of 1, 2, 3, 4-tetrahydro-3-hydroxy-7,8-benzoquinoline yields the O-derivatives first.

2. The oxidation of 1, 2, 3, 4-tetrahydro-3-hydroxy-7,8-benzoquinoline by the Oppenauer method gives 3-hydroxy-7,8-benzoquinoline. An explanation of such a reaction course was offered, involving the disproportionation of dihydro-3-hydroxy-7,8-benzoquinoline, a tautomer of 1, 2, 3, 4-tetrahydro-3-oxo-7,8-benzoquinoline.

## LITERATURE CITED

[1] P. P. Shorygin and V. N. Belov, J. Gen. Chem., 5, 1707 (1935).

[2] Organic Reactions, Vol. VI, p. 235 (1953).*

[3] R. E. Lutz, R. H. Jordan, and W. L. Truett, J. Am. Chem. Soc., 72, 4085 (1950).

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* Original Russian pagination. See C.B. Translation.

[4] H. Lange, I. G. Farbenindustrie, Zetco Reports, FIAT, Microfilm, C 60, PBL 64079.

[5] N. N. Vorozhtsov, Jr. and S. I. Kutkevichus, J. Gen. Chem., 27, 2150 (1957).*

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* Orginal Russian pagination. See C. B. Translation.

# OXOCYCLOTAUTOMERISM OF DI-β-HYDROXYETHYLAMINOACETONE

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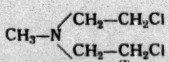
In order to prepare antitumor substances, we investigated the reaction between bromoacetone (or chloroacetone) and diethanolamine, which could result in the synthesis of di-β-hydroxyethylaminoacetone (II). Compound (II) could then be used for preparing analogs of methyl-di-β-chloroethylamine (embiquine) (I), which possesses antitumor activity.

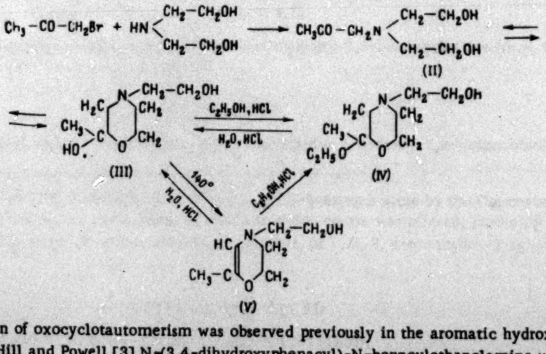


$CH_3{-}N\begin{smallmatrix}CH_2{-}CH_2Cl\\CH_2{-}CH_2Cl\end{smallmatrix}$

(I)

The reaction between α-haloketones of the aliphatic series and β-hydroxyethylamines has not been studied up to now; in the aromatic series, however, condensation of α-chloroketones (ω-chloroacetophenone) with monoethanolamine or diethanolamine results, according to the literature data, in the formation of hydroxyaminoketones (β-hydroxyethylaminoacetophenone or di-β-hydroxyethylaminoacetophenone [1-2]).

The reaction between bromoacetone (or chloroacetone) and diethanolamine gave a crystalline substance with m.p. 67-68°, which, according to its chemical properties, was a cyclic semiacetal — 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III). In solution, the cyclic semiacetal was in equilibrium with the tautomeric oxo-form — di-β-hydroxyethylaminoacetone (II). This was shown in an investigation of the ultraviolet and infrared spectra of a chloroform solution of the substance, as absorption bands, characteristic of a carbonyl group appeared on the spectra. The absorption intensity in the ultraviolet spectrum exceeded the intensity of the absorption band of acetone (see Fig.); the intensity of the absorption band in the infrared spectrum was approximately 3 times lower than the absorption band of acetone.* (Acetone had an intensity of 1.300, the substance — 0.402).



$CH_3-CO-CH_2Br$ + $HN\langle$ $CH_2-CH_2OH$ $CH_2-CH_2OH$
$CH_3CO-CH_2N\langle$ $CH_2-CH_2OH$ $CH_2-CH_2OH$
(II)
(III)
$C_2H_5OH, HCl$
$H_2O, HCl$
(IV)
140°
$H_2O, HCl$
$C_2H_5OH, HCl$
(V)

The phenomenon of oxocyclotautomerism was observed previously in the aromatic hydroxyaminoketone series. According to Hill and Powell [3] N-(3,4-dihydroxyphenacyl)-N-benzoylethanolamine underwent reversible cyclization and dehydration into 2-(3',4'-dihyroxyphenyl)-4-benzoyl-5,6-dihydro-1,4-oxazine. Lutz et al. also studied the tautomeric conversion of α-(β-hydroxyethylamino)-desoxybenzoins [4] and α-(β-hydroxyethylamino)-4,4'-dichlorodesoxybenzoins [5] into the corresponding diphenyl substituted morpholine compounds. Cromwell [6], Lutz and Jordan [7, 8] described simultaneously the cyclo-chain tautomerism of α-(ethylethanolamino)-acetophenone.

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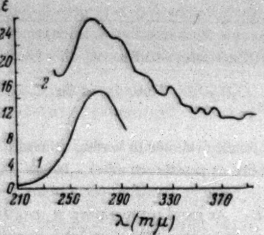
* The spectral investigation was carried out in the Optical Laboratory of the Institute of Organic Chemistry of the Academy of Sciences USSR.



Ultraviolet absorption spectrum. 1) Acetone, 2) tautomeric mixtures of di-β-hydroxyethylamino-acetone and 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (1 mole/liter).

The 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III) we prepared was a comparatively stable compound. It did not change after long storage and after boiling in benzene or aqueous solutions and it was stable to dilute acids and alkalis. (III) was dehydrated by slow distillation in vacuum and was converted into 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 (V).

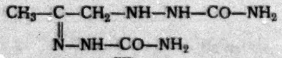
The hydrochloride, obtained by passing hydrogen chloride into an ether solution of (III), was esterified by heating in an ethanol solution to give the hydrochloride of the ethyl acetal — 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine (IV). 2-Methyl-2-methoxy-4-β-hydroxyethylmorpholine was prepared similiarly. Under these conditions propyl alcohol did not react with the hydroxy compound (III). The ethoxy compound (IV) was readily hydrolyzed back into the hydroxy compound (III).

2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III) may be distilled in vacuum if the distillation is rapid. With slow distillation, however, or on heating at 135-140° the hydroxy compound (III) eliminated water and was converted into 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 (V). The compound obtained was readily converted into the original (III) by boiling with dilute acid.

Acetal (IV) was formed by heating the dihydrooxazine compound (V) with an alcohol solution of hydrogen chloride.

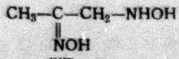
The cyclic compounds (III), (IV), and (V) do not give oximes and semicarbazones. Treatment of these compounds with semicarbazide gave, at different rates, the same solid substance with a large nitrogen content (about 45%). This compound was formed from 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III) after several hours, at room temperature; from (V) after standing for 24 hours, and its formation from the acetal (IV) required 6 hours heating. Treatment of (III) with hydroxylamine gave a colorless, crystalline compound with m.p. 153-154°.

The compounds obtained by reacting (III) with semicarbazide and hydroxylamine were not investigated thoroughly. However, from analysis data we consider it likely that they correspond to formulas (VI) and (VII).



$$\begin{array}{l} CH_3{-}C{-}CH_2{-}NH{-}NH{-}CO{-}NH_2 \\ \qquad\;\, \| \\ \qquad\;\, N{-}NH{-}CO{-}NH_2 \end{array}$$

(VI)



$$\begin{array}{l} CH_3{-}C{-}CH_2{-}NHOH \\ \qquad\;\, \| \\ \qquad\;\, NOH \end{array}$$

(VII)

Under certain conditions the cyclic form may open. Thus, similiarly to α-hydroxyketones and α-aminoketones, at room temperature the hydroxy compound (III) readily reduced Fehling's solution and an ammonia solution of silver oxide, after standing for a long period. Like all compounds containing the $CH_3$—CO-group, III gave an iodoform reaction.

All three compounds (III), (IV), and (V) were formed by condensing bromoacetone with diethanolamine in an alcohol medium, followed by distillation of the reaction products.

The reaction between α-haloketones of the aliphatic series and β-hydroxyethylamines, proceeds very smoothly, as the example investigated showed, and may be of practical value for the preparation of various aliphatic derivatives of morpholine in order to investigate their physiological and, in particular, antitumor activity [4, 9].

## EXPERIMENTAL

2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III). 50 g (0.36 mole) of bromoacetone was added with stirring over a period of 1.5 hours to 77 g (0.75 mole) of molten diethanolamine. The reaction proceeded with the evolution of heat; the temperature of the reaction mixture was kept within the range 40-50° by external cooling. The dark red reaction mixture obtained was left at room temperature until the next day. Then the mixture was heated to 50° for 1 hour and extracted several times with a large amount of ether. After distilling off the solvent, we obtained a yellowish oil, which set on cooling to a paraffin-like mass with m.p. 58-62°. The yield was 55 g (93%). After two recrystallizations from acetone, the substance had m.p. 67-68°.

The substance did not change during a rapid distillation:

B. p. 135.5-136.5° (6 mm), $n_D^{20}$ 1.4847, $d_4^{20}$ 1.1333, $MR_D$ 40.75; Calc. 40.81.

Found %: C 52.18; H 9.34; N 8.82; $H_{active}$ 1.15. M 168. $C_7H_{15}O_3N$. Calculated %: C 52.17; H 9.31; N 8.69; $H_{active}$ 1.25. M 161.

2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine was very readily soluble in water, alcohols, benzene, acetone and ethyl acetate; poorly soluble in ethyl ether and insoluble in petroleum ether. It was stable on long storage at room temperature; it was almost unchanged on boiling in benzene solution for 3 hours and boiling in aqueous solution for 2 hours. It was stable to dilute acids and alkalis. At room temperature it readily reduced Fehling's solution and also an ammonia solution of silver oxide to form a silver mirror on long standing. It gave an iodoform reaction (the iodoform had m.p. 119-121°). The same result was obtained on condensing diethanolamine with chloroacetone.

The action of semicarbazide on 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine. A mixture of 1 g of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine, 0.7 g of semicarbazide hydrochloride, 0.7 g of potassium acetate and 3 ml of water was left at room temperature for 6 hours. The precipitate was recrystallized twice from dilute alcohol. The substance (VI) obtained had a yellowish color and m.p. 253° (decomp.). It was very poorly soluble in water and alcohols.

Found %: C 31.77; H 5.53; N 45.21. $C_5H_{12}O_2N_6$. Calculated %: C 31.91; H 6.42; N 44.66.

The action of hydroxylamine on 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine. A mixture of 1 g of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine, 1 g of hydroxylamine hydrochloride, 6 ml of water and 4 ml of 10% sodium hydroxide solution was heated to boiling for 20 minutes and cooled with ice water. After recrystallization from alcohol, the crystalline precipitate (VII) had m.p. 153-154°.

The substance was readily soluble in water, alcohols and ether.

Found %: C 34.55; H 7.74; N 26.74; $H_{active}$ 1.87. M 103.5. $C_3H_8O_2N_2$. Calculated %: C 34.61; H 7.75; N 27.02; $2H_{active}$ 1.92. M 104.

2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine hydrochloride. A stream of dry hydrogen chloride was passed into a cooled ether solution of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine. The hydrochloride was precipitated quantitatively. After recrystallization from a mixture of alcohol and ether, the substance had m.p. 124-125°.

Found %: C 42.59; H 8.33; N 6.87; Cl 17.56. $C_7H_{16}O_3NCl$. Calculated %: C 42.52; H 8.16; N 7.12; Cl 17.93.

The hydrochloride dissolved in water and alcohols. On recrystallization from ethyl alcohol, the hydrochloride was partly (~ 10 - 15%) converted into 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine (IV) hydrochloride (see below). On recrystallization from isopropyl alcohol, the hydrochloride of (III) was unchanged. On adding potassium hydroxide to an aqueous solution of the hydrochloride of (III), the original base was liberated.

2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine methiodide. This was prepared by mixing equimolecular proportions of (III) and methyl iodide. After recrystallization from alcohol, the substance had m.p. 128-129°.

The methiodide was readily soluble in water and alcohols and insoluble in ether.

Found %: C 31.96; H 5.69; N 4.42. $C_{18}H_{18}O_3NI$. Calculated %: C 31.68; H 5.94; N 4.62.

2-Methyl-2-ethoxy-4-β-hydroxyethylmorpholine hydrochloride. A mixture of 2 g of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine hydrochloride, 2 ml of anhydrous ethyl alcohol and 0.5 ml of alcohol, saturated with hydrogen chloride, was boiled for 1 hour. Then ether was added dropwise to the cooled solution until turbidity appeared and the mixture obtained was placed in a refrigerator overnight. After 2 recrystallizations from a mixture of anhydrous alcohol and ethyl ether, the substance obtained formed lustrous plates with m.p. 128-129°. The yield was 65 %. The hydrochloride was very readily soluble in water and alcohols and was hygroscopic.

Found %: C 47.98; H 8.85; N 6.31; Cl 15.62. $C_9H_{20}O_3NCl$. Calculated %: C 47.89; H 8.92; N 6.21; Cl 15.71.

2-Methyl-2-ethoxy-4-β-hydroxyethylmorpholine (IV). An aqueous solution of 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine hydrochloride was saturated with potassium carbonate, the base extracted with ether, the extract dried with potassium carbonate, the ether distilled off and the residue distilled. The substance obtained had:

B. p. 101-101.5° (6 mm), $n_D^{20}$ 1.4683, $d_4^{20}$ 1.0550, $MR_D$ 49.83; calc. 50.32.

Found %: C 57.08; H 10.09; N 7.60; $H_{active}$ 0.58. M 196. $C_9H_{19}O_3N$. Calculated %: C 57.14; H 10.05; N 7.41; $H_{active}$ 0.53. M 189.

2-Methyl-2-ethoxy-4-β-hydroxyethylmorpholine was a colorless, mobile liquid with a weak smell. On storing at room temperature it became yellow. It was readily soluble in water and the usual organic solvents. It did not reduce Fehling's solution at room temperature.

On boiling semicarbazide with 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine for 6 hours, we obtained the same substance as that given by (III) with semicarbazide.

2-Methyl-2-ethoxy-4-β-hydroxyethylmorpholine methiodide. This was prepared in the same way as the methiodide from (III). The crystals had m.p. 150-151° (from ethyl alcohol). The methiodide was readily soluble in water and alcohols, but insoluble in diethyl ether.

Found %: C 36.25; H 6.65; N 4.23. $C_{10}H_{22}O_3NI$. Calculated %: C 35.95; H 6.82; N 4.07.

Hydrolysis of 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine. A solution of 1.3 g of (IV) in 3 ml of 20 % hydrochloric acid was heated for 30 minutes at 50°, then neutralized with potassium carbonate and extracted with ether. After the solvent had been distilled off, we obtained 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (III). The yield was almost quantitative.

2-Methyl-2-methoxy-4-β-hydroxyethylmorpholine hydrochloride. A mixture of 2 g of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine hydrochloride, 4 ml of methyl alcohol and 0.5 ml of methyl alcohol, saturated with hydrogen chloride, was boiled for 1 hour. After cooling, ether was added to the mixture until turbidity was produced and the mixture obtained was left overnight in a refrigerator. After 2 recrystallizations from a mixture of methyl alcohol and ether, the precipitated substance had m.p. 125.5-126.5°. The yield was 50 %. The hydrochloride was very readily soluble in water and alcohols.

Found %: C 45.63; H 8.76; N 17.02. $C_8H_{18}O_3NCl$. Calculated %: C 45.39; H 8.57; N 16.75.

2-Methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 (V). 51 g of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (m.p. 60-62°) was distilled in vacuum 4 times from a Favorsky flask. We obtained a fraction with b. p. 59-60° at 6 mm, which weighed 36.7 g ($n_D^{20}$ 1.4710). The same result was obtained on heating (III) at 135-140° for 1 hour and then distilling the product in vacuum. The product obtained changed on standing: it became yellow, the viscosity increased, the refractive index changed and reached a value of 1.4810, and crystals with m. p. 86-89° separated. The latter compound was not examined. On passing gaseous hydrogen chloride into an ether solution of the product obtained, two types of crystals separated: 1) white, flocculent flakes of a very hygroscopic hydrochloride, which was not examined; 2) fine crystals of a nonhygroscopic hydrochloride. Ethyl alcohol was added to the mixture of hydrochlorides and the nonhygroscopic hydrochloride, which did not dissolve, was filtered off (m.p. 155-158°) and recrystallized from a mixture of alcohol and ether. The substance obtained had m.p. 159-160° and was 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 (V) hydrochloride. The yield was 45 %. On separating the mixture of hydrochlorides with isopropyl alcohol, the yield of (V) hydrochloride was raised to 60 %.

Found %: C 46.87; H 7.72; N 8.04. $C_7H_{14}O_2NCl$. Calculated %: C 46.78; H 7.85; N 7.80.

The hydrochloride was readily soluble in water and less soluble in ethyl and isopropyl alcohols.

Potassium carbonate was added to an aqueous solution of 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 hydrochloride until it was saturated. The oil, which separated, was extracted with ether, dried and distilled, after distilling off the solvent.

B. p. 58.5-59° (5 mm), $n_D^{20}$ 1.4785, $d_4^{20}$ 1.1163, $MR_D$ 36.35; calc. 38.97.

On standing in a refrigerator, the substance crystallized in the form of transparent plates, m.p. 19°; they were readily soluble in water and organic solvents.

Found %: C 58.64; H 9.25; N 9.74. $C_7H_{13}O_2N$. Calculated %: C 58.74; H 9.15; N 9.78.

2-Methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 (V) reacted with methyl iodide to give a methiodide with m.p. 219-220°. The methiodide was readily soluble in water and alcohol, but insoluble in ethyl ether.

Found %: C 33.74; H 5.62; N 5.23; I 44.63. $C_8H_{16}O_2NI$. Calculated %: C 33.74; H 5.65; N 4.92; I 44.53.

We obtained a picrate from (V), as yellow needles with m.p. 153-154°.

Found %: C 42.21; H 4.61; N 15.27. $C_{13}H_{16}O_9N_4$. Calculated %: C 41.94; H 4.33; N 15.05.

On treating (V) with semicarbazide for 24 hours at room temperature the same substance was formed as in treating (III) and (IV) with semicarbazide.

*Hydration of 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 hydrochloride.* An aqueous solution of 1 g of the hydrochloride was boiled for 1 hour. The solution was then neutralized with dry potassium carbonate and extracted with ether. After evaporating off the ether, we isolated 0.8 g of crystals of 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine with m.p. 64-66° (90%). A mixture of the substance obtained with a sample of (III) did not show depression of the melting point.

Hydration of the base (V) occurred on heating with 5 % hydrochloric acid for 30 minutes. The yield of (III) was 90 %.

*Addition of alcohol to 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4.* 2 ml of anhydrous ethyl alcohol, containing hydrogen chloride, was added to 0.5 g of 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 hydrochloride. The mixture obtained was boiled for 1 hour, when all the hydrochloride gradually went into solution. The solution was evaporated down to a small volume and then ether was added to it until turbidity appeared. Crystals of 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine hydrochloride precipitated. The yield was almost quantitative.

*Condensation of bromoacetone with diethanolamine in an alcohol medium.* 50 g (0.36 mole) of bromoacetone in 50 ml of ethyl alcohol was added dropwise with stirring over a period of 1.5 hours to a solution of 76.6 g (0.75 mole) of diethanolamine in 75 ml of anhydrous ethyl alcohol. The reaction proceeded with the evolution of heat. The color of the mixture changed from pale yellow to dark red. After standing overnight, the mixture was heated for 20 minutes on a water bath. The ethyl alcohol was distilled off and the thick, brown oil remaining was extracted several times with dry ether. After evaporating off the ether, 46 g of a light brown oil was left. The product was fractionally distilled in vacuum from a Favorsky flask. We obtained 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine (~20%), 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine (~25%) and a constant boiling mixture with b.p. 58-59° at 5 mm (~25%), from which we isolated 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4 in the form of the hydrochloride (yield 35-40 %).

## SUMMARY

1. The reaction between bromoacetone (or chloroacetone) and diethanolamine was investigated. It was found that the di-β-hydroxyethylaminoacetone first formed underwent tautomeric conversion into the cyclic semiacetal — 2-methyl-2-hydroxy-4-β-hydroxyethylmorpholine.

2. 2-Methyl-2-hydroxy-4-β-hydroxyethylmorpholine was dehydrated by heating to give 2-methyl-4-β-hydroxyethyl-5,6-dihydrooxazine-1,4. The latter added alcohol and was converted into 2-methyl-2-ethoxy-4-β-hydroxyethylmorpholine. This compound was also prepared by treating the cyclic semiacetal with alcohol.

## LITERATURE CITED

[1] K. Brighton, E. Reid, J. Am. Chem. Soc. 65, 479 (1943).

[2] U.S. Pat. 2404691 (1946).

[3] R. Hill and G. Powell, J. Am. Chem. Soc. 67, 1462 (1945).

[4] R. Lutz and J. Freek, J. Am. Chem. Soc. 70, 2015 (1948).

[5] R. Lutz and R. Murphey, J. Am. Chem. Soc. 71, 478 (1949).

[6] N. Cromwell and K. Tsov, J. Am. Chem. Soc. 71, 993 (1949).

[7] R. Lutz and R. Jordan, J. Am. Chem. Soc. 71, 996 (1949).

[8] R. Jordan and R. Lutz, J. Am. Chem. Soc. 72, 1409 (1950).

[9] J. Leiter and J. Hartwell, J. Natl. Cancer. Inst. 14, 645 (1953).

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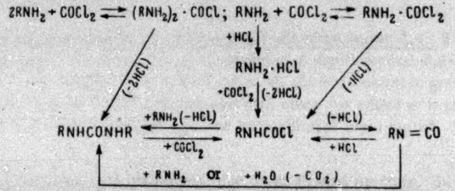
# INVESTIGATION OF SYNTHESES AND CONVERSIONS IN THE DIARYLUREA SERIES

## I. SYNTHESIS OF DIARYLUREAS AND THEIR DERIVATIVES

D. F. Kutepov and N. S. Rozanova

Diarylureas and their derivatives have found wide application in the aniline dye and chemopharmaceutical industry, in the plastics and rubber industries and in the manufacture of insecticides and fungicides. Certain diarylurea derivatives were found to be active against moths and other pests.

The method of phosgenation of aromatic amines is outstanding among the various methods of preparing diarylureas. In many cases this method is the only suitable and economically sound one. The reaction of aromatic amines with phosgene proceeds in a very complicated manner. It is known from the literature data [1] that in the phosgenation of amines, various conversions take place depending on the conditions under which the reaction occurs. The main reactions may be shown by the following scheme



This scheme shows that for the phosgenation process to proceed in the required direction, suitable conditions must be created. The phosgenation of aromatic amines is practically an irreversible reaction; therefore the diarylurea yields are often extremely high and sometimes close to quantitative. Besides that, the diarylurea yield depends to a great extent on the rate of the phosgenation reaction. In an aqueous medium the rate of the reaction of phosgene with aniline is greater than the rate of phosgene hydrolysis by water.

A. E. Kretov [3] found that the reaction of phosgene with aniline in an aqueous medium was practically complete in less than one minute. It is known that the majority of phosgenation reactions occur instantaneously but some reactions proceed relatively slowly. We established [4] that the rate of phosgenation is affected by temperature conditions, phase state of the reacting systems and the removal of hydrogen chloride from the reaction sphere. Aromatic amines are often phosgenated in organic solvents (toluene, xylene, nitrobenzene, chlorobenzene, dichloroethane etc.). This method makes it possible to prepare diarylurea from aromatic amines that are poorly soluble or emulsify with difficulty in water and the yields of the diarylureas thus obtained are usually quite high.

We investigated the phosgenation of various aromatic amines in an aqueous alkali medium and also in a medium of inert organic solvents. Phosgenation of aniline and o-anisidine in an aqueous alkali medium gave diarylurea yields that were close to quantitative. At the same time the diarylurea yield in the phosgenation of p-nitroaniline in an aqueous alkali medium was very low (8.5 %). The high diarylurea yields from the phosgenation of aniline and o-anisidine were, apparently, due to the capacity of these amines to form an emulsion with water, which ensured close contact between the amine and phosgene. On the other hand, the rate of phosgenation depends on the nature of the amine itself and increases with an increase in the amine's basicity. Thus, in the phosgenation of nitro-substituted anilines, in spite of using an excess of phosgene (20 %), the diarylurea yields were in all cases considerably less than in the phosgenation of amines with stronger basic properties (aniline, o-anisidine, p-anisidine, o-toluidine). Phosgenation of p-nitro-o-toluidine with a ratio of 1 mole of phosgene to 1 mole of amine gave a diarylurea yield of only 79.6 %.

The structure of the amines and the configuration of their molecules also affect the reaction of aromatic amines with phosgene. It appears to us that the relatively high diarylurea yields in the phosgenation of aniline as compared with o-toluidine and o-anisidine and also the greater diarylurea yields in the phosgenation of p-nitroaniline as compared with p-nitro-o-toluidine and other anilines, substituted in the ortho position, may be explained by the degree of spatial accessibility of the amine's nitrogen atom to the phosgene molecule. The removal of the hydrogen chloride formed in the reaction with various types of reagents is of great importance in the phosgenation of aromatic amines. We showed in our previous work [5] that by removing hydrogen chloride from the reaction sphere with vacuum during phosgenation of trichloroaniline, the reaction proceeded at 30° mainly in the direction of trichlorophenyl isocyanate formation. On reacting hydrogen chloride with trichlorophenylcarbanyl chloride at an even higher temperature trichloroaniline and phosgene were formed and further reaction of the two gave hexachlorodiphenylurea.

## EXPERIMENTAL

Diphenylurea. Diphenylurea was prepared by phosgenation of aniline in an aqueous alkaline medium. 11.7 g (110 %) of phosgene was passed over a period of 45 minutes into a mixture of 20 g of aniline and 150 ml of water at 20°, which was stirred vigorously. During the whole process, the reaction mixture was kept alkaline by adding sodium carbonate until there was a clear alkaline reaction to litmus. After passing in the phosgene, the reaction mixture was stirred for 1 hour at 40°. The diphenylurea formed separated as a white, finely crystalline powder. The contents of the flask were poured into a 10 % solution of hydrochloric acid and the precipitate filtered off, washed with water till neutral to litmus and dried at 80°. We obtained 22.68 g (99.4 %, calculated on the aniline) of diphenylurea with m.p. 239°.

Found %: C 72.86; 73.24; H 5.22, 5.20; N 12.76, 13.40. $C_{13}H_{12}ON_2$. Calculated %: C 73.58; H 5.66; N 13.20.

2,2'-Dinitrodiphenylurea. The phosgenation of o-nitroaniline was performed in toluene. 9.3 g of phosgene (130 %) was passed over a period of 35 minutes into a mixture of 20 g of o-nitroaniline and 150 ml of toluene at 100°, which was stirred. To bind the hydrogen chloride, sodium carbonate was introduced (110 % of the theoretical amount). On adding the phosgene, no precipitate formation was observed. After passing in the phosgene, the reaction mixture was stirred at 100° for a further 1 hour. Then the contents of the flask were cooled to 25° and 15 ml of water was added. The pale yellow precipitate formed was filtered off and recrystallized from benzene. We obtained 17.7 g (80.89 %, calculated on the o-nitroaniline) of 2,2'-dinitrodiphenylurea with m.p. 225°, which corresponds with the literature data.

Found %: C 51.42, 50.96; H 2.82, 3.24; N 17.64, 18.41. $C_{13}H_{10}O_5N_4$. Calculated %: C 51.65; H 3.31; N 18.54.

3,3'-Dinitrodiphenylurea. a) Phosgenation of m-nitroaniline in toluene. A solution of 20.1 g of m-nitroaniline in 150 ml of toluene was treated with 9.3 g (130 %) of phosgene at 100°, as in the previous experiment. The yellow, crystalline precipitate formed was filtered off and recrystallized from alcohol. We obtained 18.8 g (85.87 %) of 3,3'-dinitrodiphenylurea with m.p. 242°.

b) Phosgenation of m-nitroaniline in nitrobenzene. Ina reaction flask we placed 20 g of m-nitroaniline and 150 ml of nitrobenzene. At 40°, 9.3 g (130 %) of phosgene was passed at a rate of 0.27 g/ min. Sodium carbonate was added to combine with the hydrogen chloride. After passing in the phosgene, the temperature was raised to 70° and the reaction mixture was stirred for 1 hour. The yellow precipitate formed was filtered off and transferred to a flask, to which was added 150 ml of nitrobenzene. The contents of the flask were heated on a boiling water bath under reflux for 30 minutes, then the nitrobenzene and unreacted m-nitroaniline were distilled off in steam. The residual precipitate was filtered off, washed with 10 % hydrochloric acid then water and dried. We obtained 17.4 g (79.52 %) of 3,3'-dinitrodiphenylurea with m.p. 240°.

Found %: C 50.84, 51.36; H 3.26, 3.05; N 18.47, 18.23. $C_{13}H_{10}O_3N_4$. Calculated %: C 51.65; H 3.31; N 18.54.

4,4'-Dinitrodiphenylurea. a) Phosgenation of p-nitroaniline in an aqueous alkali medium. An aqueous suspension, previously prepared from 20 g of p-nitroaniline and 150 ml of water, was placed in a reaction flask. The mixture was heated to 40° and at this temperature, 9.3 g (130 %) of phosgene was introduced at a rate of 0.27 g/ min. During the phosgenation sodium carbonate was added to the reaction mixture so that the reaction remained neutral the whole time. After passing in the phosgene, the mixture was stirred at 70° for 1 hour, then cooled and the precipitate filtered off, washed with 10 % hydrochloric acid then water and dried. We obtained 4.6 g (18.5 %) of 4,4'-dinitrodiphenylurea with m.p. 310°.

b) Phosgenation of p-nitroaniline in nitrobenzene. 20 g of p-nitroaniline and 150 ml of nitrobenzene were placed in a flask and 9.3 g (130 %) of phosgene was passed in under the same conditions as in the phosgenation of m-nitroaniline in nitrobenzene. We obtained 20.04 g (91.5 %, calculated on the p-nitroaniline) of 4,4'-dinitrodiphenylurea with m.p. 312°.

Found %: C 51.5, 50.94; H 3.82, 3.60; N 17.64, 19.44. $C_{13}H_{10}O_5N_4$. Calculated %: C 51.65; H 3.31; N 18.54.

2,2'-Dimethoxydiphenylurea. The phosgenation of o-anisidine was carried out in an aqueous alkali medium by the method described by us previously [4]. 9.2 g (115 %) of phosgene was introduced at a rate of 0.27 g/ min into a mixture of 20 g of o-anisidine and 150 ml of water at 25°. During the phosgenation the reaction medium was kept slightly alkaline by the periodic addition of sodium carbonate (110 % of the amount required to combine with the hydrogen chloride). We obtained 21.84 g (98.8 %, calculated on the o-anisidine) of 2,2'-dimethoxydiphenylurea. The m.p. was 186°, which corresponds with literature data.

Found %: C 66.31, 66.29; H 6.15, 6.48; N 10.64, 13.30. $C_{15}H_{16}O_2N_2$. Calculated %: C 66.17; H 5.84; N 10.29.

4,4'-Dimethoxydiphenylurea. The phosgenation of p-anisidine was carried out in nitrobenzene. 9.2 g (115 %) of phosgene was passed at a rate of 0.27 g/ min into a solution of 20 g of p-anisidine in 150 ml of nitrobenzene at 40°, which was stirred. The reaction medium was kept alkaline (to Brilliant Yellow paper) by adding sodium carbonate. 10 minutes after the beginning of phosgene introduction, white crystals began to form. After passing in the phosgene, the reaction mixture was stirred at 70° for 1 hour. The isolation of the final product was the same as in the phosgenation of m-nitroaniline and p-nitroaniline in nitrobenzene. We obtained a white crystalline product with m.p. 240°; after recrystallization from alcohol, the m.p. was 242°. The weight of dry 4,4'-dimethoxydiphenylurea was 20.75 g (94.1 %).

Found %: C 65.81, 66.04; H 5.94, 6.16; N 11.02, 10.45. $C_{15}H_{16}O_3N_2$. Calculated %: C 66.17; H 5.84; N 10.29.

2,2'-Dimethyldiphenylurea. The phosgenation of o-toluidine was carried out in nitrobenzene. Into the flask was introduced 20 g of o-toluidine, 150 ml of nitrobenzene and 9.5 g (115 %) of phosgene. The experiment was carried out as in the phosgenation of other aromatic amines in nitrobenzene. After removing unreacted o-toluidine, we obtained white crystalline 2,2'-dimethyldiphenylurea with m.p. 250°. The weight of the dry product was 21.45 g (95.2 %).

Found %: C 74.97, 75.10; H 6.38, 6.46; N 11.80, 11.48. $C_{15}H_{16}ON_2$. Calculated %: C 75.02; H 6.66; N 11.66.

4,4'-Dinitro-2,2'-dimethyldiphenylurea. This compound was prepared by treating p-nitro-o-toluidine with phosgene in nitrobenzene. 24.5 g (0.25 mole) of phosgene was introduced at a rate of 0.27 g/ min into a mixture of 38.02 g (0.25 mole) of p-nitro-o-toluidine and 300 ml of nitrobenzene. The experiment was carried out as in the phosgenation of m- and p-nitroaniline in nitrobenzene. We obtained 32.96 g (79.6 %) of 4,4'-dinitro-2,2'-dimethyldiphenylurea. After washing with 20 % hydrochloric acid and water, the substance obtained melted at 300°, which corresponds with the literature data.

## SUMMARY

1. We described the preparation of a series of diarylureas in high yields by the phosgenation of aromatic amines both in an aqueous medium and in a medium of inert organic solvents.

2. A scheme for the possible conversions in the reactions of aromatic amines with phosgene is given.

## LITERATURE CITED

[1] R. P. Lastovsky, J. Appl. Chem. 19, 440 (1946); J. Gen. Chem. 18, 921 (1948); V. A. Rudenko, A. Ya. Yakubovich and T. Ya. Nikiforova, J. Gen. Chem. 17, 2256 (1947); Shriner, J. Am. Chem. Soc. 53, 1603 (1931); Horne and Shriner, J. Am. Chem. Soc. 53, 3186 (1931); Brit. Pat. 17123: Ch. A. 9, 383 (1915); Hentschel, Ber. 17, 1284, (1884); Fieser and Creech, J. Am. Chem. Soc. 61, 3502 (1939); Hentschel, Ber. 18, 1178 (1885); Michler and Zimmerman, Ber. 12, 1166 (1879), 14, 2177 (1881); Hentschel, Ber. 17, 1284 (1884); Germ. Pat. 241822; Frdl. 10, 656.

[2] Vles, Rec. trav. chim. 53, 961 (1934).

[3] A. E. Kretov, J. Appl. Chem. 2, 483 (1929).

[4] D. F. Kutepov, Z. G. Vukolova, J. Gen. Chem. 24, 698 (1954).*

[5] D. F. Kutepov, N. S. Rozanova, J. Gen. Chem. 26, 1737 (1956).*

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* Original Russian pagination. See C.B. Translation.

# CHEMISTRY OF SELENOPHENE

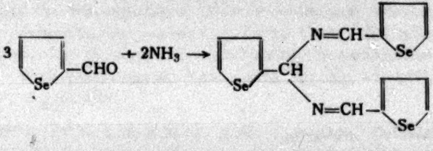
## VIII. N-(SELENENAL*-2)-AMINES, 2-PHENYL-4-(SELENENAL-2)-OXAZOLONE-5, 5-(SELENENAL-2)-THIAZOLIDON-4-THIONE-2 (SELENENAL-2-RHODANINE) AND SELENOPHEN-2-ALDEHYDE HYDRAZOTHIAZOLINONE

Yu. K. Yurev, N. N. Mezentsova and T. A. Balashova

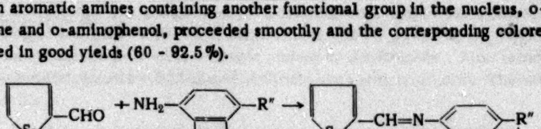
We reported in a previous paper [1] that selenophen-2-aldehyde underwent reactions charactristic of aldehydes of the aromatic series, such as the Cannizzaro and Perkin reactions.

In this work we studied other reactions of selenophen-2-aldehyde, characteristic of aromatic aldehydes, namely reactions with ammonia, amines and some compounds, containing active methylene groups.

We established that selenophen-2-aldehyde reacted with ammonia, like benzaldehyde or thiophen-2-aldehyde, to form the corresponding hydramide — selenenal-2-hydramide.

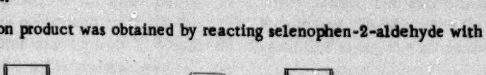


The reactions of selenophen-2-aldehyde with some of the simplest aromatic amines, aniline and α-naphthylamine, and with aromatic amines containing another functional group in the nucleus, o- and p-aminobenzoic acids, m-nitroaniline and o-aminophenol, proceeded smoothly and the corresponding colored azomethine compounds were obtained in good yields (60 - 92.5 %).



where: R = COOH, R' = H, R" = H or R = H, R' = H, R" = COOH, or R = H, R' = $NO_2$, R" = H, or R = = OH, R' = H, R" = H.

A colorless reaction product was obtained by reacting selenophen-2-aldehyde with cyclohexylamine.



The yields were somewhat lower (30-45 %) in the reactions of selenophen-2-aldehyde with the diamines, ethylenediamine and p-phenylenediamine, which gave, N,N'-di-(selenenal-2)-ethylenediamine and N,N'-di-(selenenal-2)-p-phenylenediamine.

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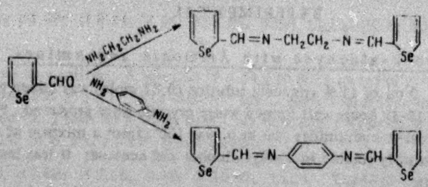
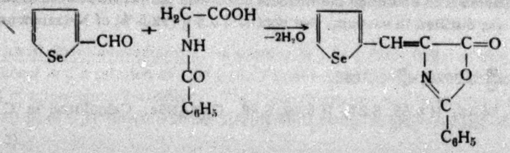
* Chemical Abstracts translates "selenenal" as "selenophenylmethylidene" – Publisher's note.

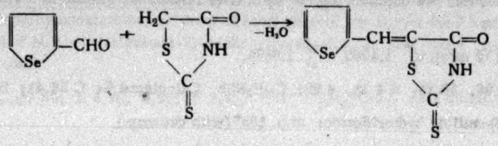


It also seemed interesting to condense selenophen-2-aldehyde with compounds containing active methylene groups, which would make it possible to prepare oxazolone or rhodanine derivatives, containing a selenophene ring.

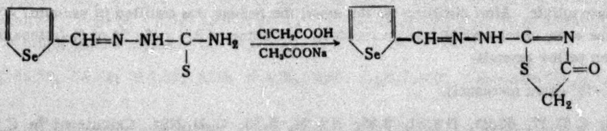
We established that selenophen-2-aldehyde condensed very readily with hippuric acid and the corresponding azlactone — 2-phenyl-4-(selenenal-2)-oxazolone-5 — was obtained in quantitative yield.



Selenophen-2-aldehyde reacted with rhodanine (thiazolidon-4-thione-2) to form selenenal-2-rhodanine, i.e. 5-(selenenal-2)-thiazolidon-4-thione-2, also in quantitative yield.



Finally, we showed that the thiosemicarbazone of selenophen-2-aldehyde condensed readily with chloroacetic acid in the presence of sodium acetate to give the hydrazothiazolinone of selenophen-2-aldehyde in good yield:



The melting points of almost all the compounds of the selenophene series prepared in this work were very close to the melting points of the compounds of the thiophen series analogous to them in structure.

The results given above, obtained in this work, show that selenophen-2-aldehyde undergoes many reactions characteristic of aldehydes possessing an aromatic nature and, in particular, thiophen-2-aldehyde. However, we observed that selenophen-2-aldehyde behaved differently from thiophen-2-aldehyde in one of the characteristic reactions. Thus, we unsuccessfully attempted to carry out a benzoin condensation of selenophen-2-aldehyde and to perform a cyanhydrin synthesis on it by N. D. Zelinsky's method, to prepare simplest α-aminoacids, containing a selenophen ring. Selenophen-2-aldehyde did not undergo benzoin condensation or cyanhydrin synthesis, but was considerably resinified and broken down with the liberation of selenium. This peculiarity should be noted as the sulfur analog of selenophen-2-aldehyde — thiophen-2-aldehyde — was shown by Cardon and Lankelma [2] to undergo benzoin condensation to form thenoin in 32 % yield.

# EXPERIMENTAL

## Reactions of Selenophen-2-aldehyde with Ammonia and Amines

Selenenal-2-hydramide. 9 ml of 11 % ammonia solution (0.07 mole) was added to 5 g (0.0314 mole) of selenophen-2-aldehyde. After 10-12 hours well formed white crystals were produced. From two experiments we obtained 3.1 g (30 %) of selenenal-2-hydramide: the m.p. was 100° (from a mixture of acetone and water in the ratio 5 : 1); the material was readily soluble in methyl alcohol and acetone; it was less soluble in ethyl alcohol and insoluble in ether and water.

Found %: C 39.23, 39.32; H 3.04, 3.03; N 5.87, 5.73. $C_{15}H_{12}N_2Se_3$. Calculated %: C 39.16; H 2.65; N 6.13.

N-(Selenenal-2)-aminocyclohexane. 2.5 g (0.025 mole) of cyclohexylamine (b.p. 129-131°, $n_D^{20}$ 1.4601), was added to 4 g (0.025 mole) of selenophen-2-aldehyde, and a considerable amount of heat was evolved. The reaction mixture was extracted with ether and the extracts dried with anhydrous sodium sulfate. After distilling off the ether the residue was distilled in vacuum. We obtained 5.6 g (92.5 %) of N-(selenenal-2)-aminocyclohexane:

b.p. 156° (8 mm), $n_D^{20}$ 1.5920, $d_4^{20}$ 1.3082.

Found %: C 54.50, 54.46; H 6.55, 6.37; N 6.06, 6.08. $C_{11}H_{15}NSe$. Calculated %: C 54.99; H 6.29; N 5.83.

N-(Selenenal-2)-aniline. 2.92 g (0.0314 mole) of aniline in 10 ml of methyl alcohol was added to a solution of 5 g (0.0314 mole) of selenophen-2-aldehyde in 5 ml of methyl alcohol, and an intense red color appeared. The reaction mixture was heated for 2 hours on a boiling water bath; then the solvent was distilled off and the residue distilled in vacuum. We obtained 5 g (70 %) of N-(selenenal-2)-aniline as a viscous, dark red liquid, which darkened rapidly in air:

b. p. 189-190° (12 mm), $d_4^{20}$ 1.4262, $n_D^{20}$ 1.6855.

Found %: C 56.96, 56.75; H 4.18, 4.29; $C_{11}H_9NSe$. Calculated %: C 56.41; H 3.87.

N-(Selenenal-2)-aniline hydrochloride: m.p. 165° (with decomp.).

Found %: N 5.58, 5.54. $C_{11}H_{10}NClSe$. Calculated %: N 5.17.

N-(Selenenal-2)-α-aminonaphthalene. 2.86 g (0.02 mole) of α-naphthylamine ( m.p. 50°) was added to 3.08 g (0.02 mole) of selenophen-2-aldehyde. On standing, the naphthylamine completely dissolved. The reaction mixture was heated for 2 hours on a water bath and then extracted with ether and the extracts dried with anhydrous sodium sulfate. After distilling off the ether, the residue was distilled in vacuum, and at 262° (12 mm) a thick oil came over, which crystallized on standing. We obtained 3.4 g (60 %) of N-(selenenal-2)-α-naphthylamine as golden yellow crystals:

m.p. 74-75° (from methanol).

Found %: C 63.17, 63.23; H 3.81, 3.85; N 5.24, 5.23. $C_{15}H_{11}NSe$. Calculated %: C 63.40; H 3.92; N 4.88.

N-(Selenenal-2)-p-aminobenzoic acid. A solution of 2.15 g (0.0155 mole) of p-aminobenzoic acid in 25 ml of ethyl alcohol was added to 2.5 g (0.0155 mole) of selenophen-2-aldehyde. Immediately a red color appeared and a red crystalline precipitate formed, which was separated off, washed with alcohol and recrystallized from glacial acetic acid. We obtained 3.63 g (83.5 %) of N-(selenenal-2)-p-aminobenzoic acid; the m.p. was 200° (with decomp.).

Found %: C 52.43, 52.29; H 3.39, 3.57; N 4.80, 5.02. $C_{12}H_9O_2NSe$. Calculated %: C 51.81; H 3.26; N 5.04.

N-(Selenenal-2)-o-aminobenzoic acid. A solution of 2.07 g (0.0158 mole) of o-aminobenzoic acid in 10 ml of methyl alcohol was added to a solution of 2.4 g (0.0158 mole) of selenophen-2-aldehyde in 5 ml of methyl alcohol and the mixture heated for 3 hours on a water bath. We obtained 3.6 g (80 %) of N-(selenenal-2)-o-aminobenzoic acid as bright red crystals; the m.p. was 132° (from alcohol):

Found %: C 51.83, 51.49; H 3.24, 3.24; N 5.49, 5.69; $C_{12}H_9O_2NSe$. Calculated %: C 51.81; H 3.26; N 5.04.

**N-(Selenenal-2)-m-nitroaniline.** A solution of 4.34 g (0.0314 mole) of m-nitroaniline in 20 ml of methyl alcohol was added to a solution of 5 g (0.0314 mole) of selenophen-2-aldehyde in 5 ml of ethyl alcohol. The reaction mixture was heated for 1 hour on a water bath. We obtained 7 g (80 %) of N-(selenenal-2)-m-nitroaniline as dirty green crystals; the m.p. was 93-94° (from alcohol).

Found %: C 47.15, 47.09; H 2.58, 2.76; N 10.43, 10.24. $C_{11}H_8O_2N_2Se$. Calculated %: C 47.32; H 2.89; N 10.04.

**N-(Selenenal-2)-o-aminophenol.** A solution of 4.3 g (0.025 mole) of selenophen-2-aldehyde and 2.95 g (0.025 mole) of o-aminophenol in 40 ml of methyl alcohol was heated for 2 hours on a water bath. We obtained 3.5 g (70 %) of N-(selenenal-2)-o-aminophenol as yellow crystals; the m.p. was 55° (from methyl alcohol).

Found %: C 52.74, 52.68; H 3.67, 3.54; N 5.58, 5.69. $C_{11}H_9ONSe$. Calculated %: C 52.81; H 3.62; N 5.59.

**N,N'-Di-(selenenal-2)-ethylenediamine.** A solution of 1.33 g (0.01 mole) of ethylenediamine hydrochloride in 20 ml of ethyl alcohol and a solution of 1.06 g (0.01 mole) of sodium carbonate in 4 ml of water were added to 3.2 g (0.02 mole) of selenophen-2-aldehyde. The reaction mixture was heated for 3 hours on a water bath. We obtained 1.1 g (30 %) of N,N'-di-(selenenal-2)-ethylenediamine as grey crystals; the m.p. was 110° (from aqueous alcohol 1 : 1).

Found %: C 42.45, 42.34; H 3.57, 3.56; N 8.40, 8.20. $C_{12}H_{12}N_2Se_2$. Calculated %: C 42.08; H 3.54; N 8.48.

**N,N'-Di-(selenenal-2)-p-phenylenediamine.** A mixture of 2 g (0.0124 mole) of selenophen-2-aldehyde, 0.7 g (0.0062 mole) of p-phenylenediamine and 3 ml of ethyl alcohol was heated for 2 hours on a water bath. We obtained 1.6 g (45 %) of N,N'-di-(selenenal-2)-p-phenylenediamine as dark yellow crystals; the m.p. was 187-188° (from butyl alcohol).

Found %: C 49.53, 49.50; H 3.26, 3.25; N 7.45, 7.31. $C_{16}H_{12}N_2Se_2$. Calculated %: C 49.26; H 3.10; N 7.18.

### Condensation of selenophen-2-aldehyde with Compounds Containing Active Methylene Groups

**2-Phenyl-4-(selenenal-2)-oxazolone-5.** A mixture of 6.8 g (0.043 mole) of selenophen-2-aldehyde, 7.63 g (0.043 mole) of hippuric acid, 3.5 g (0.043 mole) of anhydrous sodium acetate and 42.9 g(0.043 mole) of acetic anhydride was heated for 1 hour on a water bath at 60-70°. We obtained 10.4 g (80 %) of 2-phenyl-4-(selenenal-2)-oxazolone-5 as bright yellow crystals; the m.p. was 173-174° (from benzene).

Found %: C 55.73, 55.68; H 3.05, 3.09; N 4.86, 4.80. $C_{14}H_9O_2NSe$. Calculated %: C 55.64; H 3.00; N 4.63.

**5-(Selenenal-2)-thiazolidon-4-thione-2.** 8 g (0.1 mole) of anhydrous sodium acetate was added to a gently heated solution of 5.2 g (0.032 mole) of selenophen-2-aldehyde and 4.32 g (0.032 mole) of rhodanine (m.p. 162°) in 30.3 ml of glacial acetic acid; the reaction mixture boiled up and a brown precipitate was formed. The mixture was heated for a further half hour and 150 ml of water was added; the precipitate was filtered off and washed with water, alcohol and ether. We obtained 7 g (91 %) of 5-(selenenal-2)-thiazolidon-4-thione-2 as lustrous, brown crystals; the m.p. was 234°.

Found %: C 35.65, 35.63; H 1.82, 1.83; N 5.02, 4.84. $C_8H_5ONS_2Se$. Calculated %: C 35.04 ; H 1.84; N 5.11.

### Preparation of Selenophen-2-aldehyde Hydrazothiazolinone

1 g (0.014 mole) of anhydrous sodium acetate and 1 g (0.01 mole) of chloroacetic acid were added to a solution of 1.16 g (0.005 mole) of selenophen-2-aldehyde thiosemicarbazone (m.p. 176°) in 25 ml of alcohol and the mixture heated on a water bath for 1 hour. The precipitate formed was filtered off and washed with hot water

and alcohol. We obtained 1.1 g (80 %) of selenophen-2-aldehyde hydrazothiazolinone as lustrous, light yellow crystals; the m.p. was 210°.

Found %: C 35.17, 35.29; H 2.48, 2.37; N 15.16, 14.94. $C_8H_7ON_3SSe$. Calculated %: C 35.18; H 2.21; N 15.03.

## SUMMARY

1. Selenophen-2-aldehyde reacted with ammonia to give selenenal-2-hydramide.

2. Selenophen-2-aldehyde reacted with primary amines to give azomethine compounds, of which the following are described in this paper: N-(selenenal-2)-aminocyclohexane, N-(selenenal-2)-aniline, N-(selenenal-2)-aminonaphthalene, N-(selenenal-2)-p-aminobenzoic acid, N-(selenenal-2)-o-aminobenzoic acid, N-(selenenal-2)-m-nitroaniline, N,N'-di-(selenenal-2)-ethylenediamine and N,N'-di-(selenenal-2)-p-phenylenediamine.

3. Selenophen-2-aldehyde condensed with hippuric acid and with rhodanine to give 2-phenyl-4-(selenenal-2)-oxazolone-5 and 5-(selenenal-2)-thiazolidon-4-thione-2, respectively.

4. The thiosemicarbazone of selenophen-2-aldehyde condensed with chloroacetic acid to give the hydrazothiazolinone of selenophen-2-aldehyde.

## LITERATURE CITED

[1] Yu. K. Yurev and N. N. Mezentsova, J. Gen. Chem. 27, 179 (1957).*

[2] S. Z. Cardon and H. P. Lankelma, J. Am. Chem. Soc. 70, 4248 (1948).

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* Original Russian pagination. See C.B. Translation.

# REACTION OF NITROSYL CHLORIDE WITH UNSATURATED HYDROCARBONS

## III. REACTION WITH ISOPROPYLETHYLENE*

K. A. Ogloblin

The reaction of nitrosyl chloride with tri- and fully substituted ethylenes and hydrocarbons of the cyclohexene series was investigated for a large number of examples [2]. Much less is known on the reaction of nitrosyl chloride with symmetrical and unsymmetrical disubstituted ethylenes and very little on that with monosubstituted ethylenes.

In the reaction with isopropylethylene [3] a green oil was obtained which was heavier than water and whose composition was not investigated. 1,2-Dichloropropane [4] was isolated from the reaction products of nitrosyl chloride with propylene and a solid bis-nitrosochloride [5] was obtained in the presence of metallic catalysts. Nothing is said of the other reaction products. This reaction was carried out with n-hexene-1, n-heptene-1, n-octene-1 [6] and with a series of higher normal ethylene hydrocarbons with a terminal double bond [7]. In certain cases solid nitrosochlorides [7] were obtained, while the liquid reaction products were not investigated.

In reacting nitrosyl chloride with arylethylenes: styrene [4, 6, 8], 4-methylstyrene [8, 9], 2- and 3-methylstyrene [6], 2,4,6-trimethylstyrene [9] and allylbenzene [6], the investigators noted the presence [4, 6, 8] or the absence [9] of solid nitrosochlorides, while, as a rule, the liquid products were not investigated. ω-Nitrostyrene and phenyldichloroethane were found in the reaction products only in experiments with styrene [8].

It can be seen from this brief summary that the reaction of nitrosyl chloride with monoalkylethylenes has not been studied sufficiently.

In order to elucidate the course of the reaction of nitrosyl chloride with monoalkylethylenes we investigated the reaction with isopropylethylene.

The reaction was carried out with equimolecular amounts of hydrocarbon and nitrosyl chloride (or with slight excess of the hydrocarbon), in an ether solution in sealed ampules.

The reaction proceeded very slowly at a temperature of -40° to -50°, either in ether or without solvent and over a period of several hours there were no visible signs of reaction. At a temperature, close to room temperature, the reaction, without solvent, proceeded very vigorously with considerable evolution of heat and broke the ampule. The same result was achieved in experiments with concentrated solutions of the reagents in ether, without cooling.

With a ratio of 4–5 ml of ether per g of NOCl and cooling the ampule with cold water, the reaction proceeded calmly and was complete after several hours. Under these conditions, the reddish brown color of the reaction mixture changed to a light green. Strong pressure was always observed, when after cooling ( -50°), the ampules were opened.

In contrast to trimethylethylene and isobutylene, no solid nitrosochloride was formed in the reaction of nitrosyl chloride with isopropylethylene. The main reaction products were 3-chloro-4-nitro-2-methylbutane and 3,4-dichloro-2-methylbutane. Besides that, we found a small amount of an unsaturated monochloride, $C_6H_9Cl$, which was apparently 4-chloro-2-methylbutene-2. The fraction, corresponding to the dichloride, was colored a deep blue by a trace of 3-chloro-4-nitroso-2-methylbutane, which could not be separated from the dichloride by distillation. The blue color gradually disappeared when the product was kept in diffuse light and very rapidly in direct sunlight.

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* For Reports I and II see [1].

As analysis and qualitative reactions showed, the higher fractions contained the acid chloride of α-chloroisovalerohydroxamic acid mixed with a chloronitrohydrocarbon.

The course of the reaction of nitrosyl chloride with isopropylethylene may be shown by the scheme given below.

$$(CH_3)_2CH{-}CH{=}CH_2 \xrightarrow{NOCl} (CH_3)_2CH{-}CHCl{-}CH_2NO$$

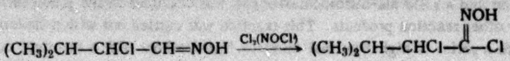
$$(CH_3)_2CH{-}CHCl{-}CH_2NO \xrightarrow{NOCl} (CH_3)_2CH{-}CHCl{-}CH_2NO_2 + Cl_2 + N_2$$

$$(CH_3)_2CH{-}CH{=}CH_2 \xrightarrow{Cl_2} (CH_3)_2CH{-}CHCl{-}CH_2Cl + C_5H_9Cl$$

On treating isopropylethylene with nitrosyl chloride, besides the addition of nitrosyl chloride, there occurred the oxidation of the nitroso group to the nitro group, which proceeded at a rate greater than that of the addition.*

The oxidation of the nitroso compound was accompanied by nitrosyl chloride decomposition giving chlorine, which gave a dichloride and some unsaturated monochloride with the hydrocarbon.

No α-chloroisovaleraldehyde oxime was found in the reaction products; consequently, under these conditions there was practically no rearrangement of the nitro compound into the oxime. It is possible that a small amount of oxime was, nevertheless, formed but was then converted into the acid chloride of α-chloroisovalerohydroxamic acid by chlorine or nitrosyl chloride [12].



$$(CH_3)_2CH{-}CHCl{-}CH{=}NOH \xrightarrow{Cl_2(NOCl)} (CH_3)_2CH{-}CHCl{-}\overset{\overset{NOH}{\|}}{C}{-}Cl$$

The structure of the chloronitrohydrocarbon was proved by preparing α-chloroisovaleric acid from it by heating it with hydrochloric acid in a sealed ampule [10].

$$(CH_3)_2CH{-}CHCl{-}CH_2NO_2 \xrightarrow{HCl,\ H_2O} (CH_3)_2CH{-}CHCl{-}COOH$$

On reducing the chloronitrohydrocarbon with zinc amalgam in hydrochloric acid at room temperature, the amount of zinc that dissolved was the amount required for reducing one nitro group to the hydroxylamino group.

Two equivalents of alkali were used in the reaction with alcoholic KOH, and potassium chloride was immediately precipitated, which indicated the lability of the chlorine atom.

## EXPERIMENTAL

Reaction of isopropylethylene with nitrosyl chloride. 125 g of nitrosyl chloride** was added with stirring to a mixture of 134 g of isopropylethylene(b.p. 19-22°, $n_D^{18.6}$ 1.3660, prepared by dehydration of isoamyl alcohol over aluminum sulfate [1] ) and 500 ml of anhydrous ether, cooled to -10°. The red-brown colored reaction mixture was poured into 17 ampules and the ampules were sealed and placed in a water bath (+3°). After 2 hours, the reaction mixture in the ampules acquired a brown color with a green tinge, which indicated that the reaction had already partly occurred. The next day the liquid in the ampules was a clear yellow-greeen and the bath temperature was +11°.

The ampules were cooled to -50° and opened by heating the ends with a naked flame and they were found to be under high pressure.

The volatile part of the reaction mixture was distilled off without heating under reduced pressure (110-65 mm) and the distillate was condensed in traps ( -50°). After two distillations, the distillate yielded 38 g of unreacted isopropylethylene with b.p. 16-21° at 778 mm, with the bulk boiling at 19.5-20.5°.

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* This is confirmed by the fact that a chloronitro compound and a dichloride were the main reaction products.

** This was prepared by passing hydrogen chloride into a heated solution of nitrosyl sulfuric acid in sulfuric acid. The product was freed from hydrogen chloride by boiling for half an hour in a flask with a reflux condenser, cooled with a mixture of solid carbon dioxide and alcohol.

The bright green liquid remaining after distilling off the volatile products was distilled from a Favorsky flask. A fraction was distilled off with b.p. 24-70° at 5 mm, which had a dark blue color and weighed 64.8 g. The residue was a light green, turbid liquid, weighing 116.7 g.

After several distillations in vacuum and then at normal pressure, the fraction 24-70° at 5 mm yielded fractions: 1st b.p. 105-108° at 766 mm, 0.85 g; 2nd b.p. 141-146° at 777 mm, 22.5 g. The bulk of the 2nd fraction (~80%) distilled at 143-146°. After several distillations, the residue weighing 116.7 g yielded fractions: 3rd b.p. 74-76° at 7 mm, 7.2 g; 4th b.p. 76-77° at 7 mm, 14.5 g; 5th b.p. 52.5-54.5° at 1 mm, 6.4 g; 6th b.p. 58° at 1 mm, 2.3 g.

Investigation of fractions. 1st fraction b.p. 105-108° at 766 mm was a colorless clear liquid, insoluble in water and decolorizing potassium permanganate solution and a solution of bromine in carbon tetrachloride.

$n_D^{20}$ 1.4353, $d_4^{20}$ 0.9799.

Found %: Cl 37.93, 37.72. $C_5H_9Cl$. Calculated %: Cl 33.92.

On treatment with potassium acetate in acetic acid, the material gave a small amount of an ester with the smell of isoamyl acetate.

The fraction was an unsaturated monochloride, apparently 2-methyl-4-chlorobutene-2 with traces of dichloride $C_5H_{10}Cl_2$.

The small amount of the material prevented careful purification.

Literature data: b.p. 107-110°, $d_4^{20}$ 0.9340 [13], $n_D^{20}$ 1.4397, $d^{20}$ 0.9218 [14].

2nd fraction with b.p. 141-146° at 777 mm. The bulk of the material distilled at 42.5-43.5° (20 mm). It was a colorless, clear, mobile liquid. It was not soluble in water.

$n_D^{20}$ 1.4475, $d_4^{20}$ 1.0805, $MR_D$ 34.91; calc. 35.02.

Found %: Cl 49.84, 49.91. $C_5H_{10}Cl_2$. Calculated %: Cl 50.28.

The fraction was the dichloride — 3,4-dichloro-2-methylbutane.

Literature data: b.p. 143-145°, $d^{17.5}$ 1.0923 [15].

3rd and 4th fractions — 3-chloro-4-nitro-2-methylbutane. This was a colorless liquid with a sharp smell and a lachrymatory vapor. It was insoluble in water, but readily soluble in the normal organic solvents.

For the 4th fraction with b.p. 76-77° at 7 mm:

$n_D^{20}$ 1.4548, $d_4^{20}$ 1.1550, $MR_D$ 35.60; calc. 35.80.

Found %: N 9.55, 9.47; Cl 24.23, 24.13.* M 150.4, 150.5. $C_5H_{10}O_2NCl$. Calculated %: N 9.24; Cl 23.39. M 151.6.

The substance did not give a qualitative reaction for a nitro group [11]; it dissolved in alkalis slowly in the cold and rapidly on heating to give a turbid yellow solution. This gave a strong aldehyde smell. On treatment with alcoholic KOH, 2 equiv. of alkali were consumed to give an immediate precipitate of potassium chloride. The substance did not change during many months storage in sealed ampules.

The nitro group content of the substance was determined by reduction to the hydroxylamine derivative with zinc amalgam.

A sample of the substance was shaken in a flask with zinc amalgam and excess dilute hydrochloric acid at room temperature. The completeness of the reaction was determined by determining the zinc ions in the solution with "trilone B."

Found %: $NO_2$ 32.0, 31.7; number of $NO_2$-groups 1.05, 1.04. $(C_5H_{10}Cl)NO_2$. Calculated %: $NO_2$ 30.3; number of $NO_2$-groups 1.00.

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* Numerous analyses of this substance, obtained in different experiments by the Carius and the semimicro Korshin methods, always gave high (by 0.7-1.0 %) chlorine contents.

Conversion of 3-chloro-4-nitro-2-methylbutane into α-chloroisovaleric acid [10]. 5.1 g of the fraction with b.p. 74-76° at 7 mm was heated with 10 ml of hydrochloric acid (d 1.19) in a sealed ampule on a boiling water bath for 6 hours.

On opening the ampules, it was found that pressure had not been generated and the substance remained unchanged, even though both layers had become yellow. The ampule was again sealed and heated for 2 hours at 130-140°. The upper layer decreased and became a brown color. The ampule was opened after cooling to minus 12-14° and considerable pressure had been generated. In the bottom of the ampule were white crystals. They were separated from the liquid and dried in a vacuum desiccator over phosphorus pentoxide. The weight was 0.5 g; the crystals were ammonium chloride.*

The oily layer was separated and washed 3 times with water. The weight was 2.73 g. It dissolved in 10% sodium hydroxide solution. On distilling in vacuum, it yielded a fraction with b.p. 68.5-71.7° at 2 mm and weighing 1.35 g, which was a colorless liquid with the smell of an organic acid. The substance crystallized on cooling; it was dried on a porous plate in a vacuum desiccator over phosphorus pentoxide. The m.p. was 37-39°. The neutralization equivalent of the substance was determined by titration with 0.1 N NaOH in an aqueous solution in the presence of phenolphthalein and the chlorine content was also determined.

Found %: Cl 26.17, 26.20. Equiv. 135.3, 136.8. $C_5H_9O_2Cl$. Calculated %: Cl 25.97. Equiv. 136.5.

Literature data [17]: m.p. 35-35.5°.

5th and 6th fractions (b.p. 52.5-54.5 and 58° at 1 mm) were a mixture of 3-chloro-4-nitro-2-methylbutane and the acid chloride of α-chloroisovalerohydroxamic acid. The presence of the acid chloride of α-chloroisovalerohydroxamic acid was proved by quantitative reactions. On heating 1 drop of the substance with 2-3 ml of water and 2-3 drops of ferric chloride solution, a pale red color appeared, which turned to a dark red color with a voilet tinge as the acid chloride was hydrolyzed (over 1 minute).

For the fraction with b.p. 58° at 1 mm: $n_D^{20}$ 1.4820, $d_4^{20}$ 1.2414, $MR_D$ 39.05; calc. 39.35.

Found %: Cl 29.40, 29.19. M 166.1, 163.4. $C_5H_9ONCl_2$. Calculated %: Cl 41.70. M 170.0. $C_5H_{10}O_2NCl$. Calculated %: Cl 23.39. M 151.6.

## SUMMARY

1. The reaction of nitrosyl chloride with isopropylethylene in an ether solution gave, as the main products, 3-chloro-4-nitro-2-methylbutane and 3,4-dichloro-2-methylbutane.

3-Chloro-4-nitroso-2-methylbutane, 4-chloro-2-methylbutene-2 and the acid chloride of α-chloroisovalerohydroxamic acid were also formed, in small amounts, in this reaction.

2. The primary reaction product, 3-chloro-4-nitroso-2-methylbutane, was oxidized by the nitrosyl chloride to 3-chloro-4-nitro-2-methylbutane while the chlorine, formed by decompsoition of the nitrosyl chloride reacted with isopropylethylene to give mainly 3,4-dichloro-2-methylbutane and a small amount of an unsaturated monochloride.

## LITERATURE CITED

[1] S. N. Danilov and K. A. Ogloblin, J. Gen. Chem. 22, 2113 (1952);** K. A. Ogloblin, J. Gen. Chem. 22, 2121 (1952).**

[2] L. Beckham, W. Fessler and M. Kise, Chem. Revs. 48, 319 (1951).

[3] V. N. Ipatev, J. Russ. Chem. Soc. 31, 426 (1899).

[4] W. Tilden and J. Sudborough, J. Chem. Soc. 63, 479 (1893).

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* According to [10], nitro derivatives of methane, ethane and propane give the corresponding carboxylic acids and hydroxylamine hydrochloride. Under the conditions of the experiment, the hydroxylamine decomposed by the equation [16]: $4NH_2OH = N_2O + 2NH_3 + 3H_2O$.

** Original Russian pagination. See C.B. Translation.

[5] U.S. Pat. 2417675; Ch. A. 41, 3478 (1947).

[6] N. Thorne, J. Chem. Soc. 1956, 4271.

[7] U. S. Pat. 2435570; Ch. A. 42, 2983d (1948).

[8] R. Perrot, C. r. 202, 494 (1936); Ch. A. 30, 4155 (1936); R. Perrot, C. r. 203, 329 (1936); Ch. A. 30, 8161 (1936).

[9] A. Klages, Ber. 35, 2245 (1902).

[10] V. Meyer and J. Locher, Lieb. Ann. 180, 163 (1876).

[11] I. Guben, Methods of Organic Chemistry, Vol. IV, 347, 359 (1949).*

[12] H. Yale, Chem. Revs. 33, 209 (1943).

[13] O. Aschan, Ber. 51, 1303 (1918).

[14] U. S. Pat. 2376396; Ch. A. 39, 3548 (1945).

[15] I. Kondakov, J. Russ. Chem. Soc. 20, 144 (1888).

[16] K. Hofmann and F. Kroll, Ber. 57 B, 937 (1924).

[17] Beilst., II, p. 316.

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* In Russian.

# THE REACTIONS OF FREE RADICALS IN SOLUTION

## XI. THE MECHANISM OF THE INHIBITING EFFECT OF QUINONES ON THE THERMAL POLYMERIZATION OF STYRENE

B. A. Dolgoplosk and D. Sh. Korotkina

It was shown in the preceding investigation [1] that phenols and aromatic amines are not in themselves inhibitors of the process of styrene polymerization. The inhibiting effect of these compounds is observed only in the presence of oxygen or heavy metal salts which are capable of oxidizing them to the corresponding quinoid compounds. Investigations by various authors of the inhibiting effect of quinones on the thermal polymerization of styrene have not as yet given a final explanation of the mechanism of this reaction. The majority of authors [2], occupied with this problem, have shown that during the induction period, caused by the presence of quinone, hydroquinone and condensation products of quinone and styrene are formed and their structure has not yet been definitely established.

This investigation was devoted to studying the mechanism of the inhibiting effect of quinones on the thermal polymerization of styrene.

## EXPERIMENTAL AND DISCUSSION OF RESULTS

Inhibiting effect of quinones on the thermal polymerization of styrene. Unlike the effect of polyphenols and aromatic amines, the inhibiting effect of quinones is characterized first of all by the fact that it does not depend qualitatively on the presence of oxygen and appears both in the presence of air and in an atmosphere of nitrogen.

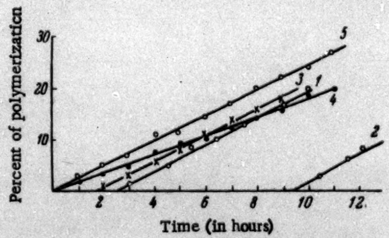


Fig. 1. The effect of different quinones on the polymerization of styrene in the absence of oxygen. 1) Benzoquinone (0.01 mole %), 2) the same (0.09 mole %), 3) naphthoquinone (0.01 mole %), 4) anthraquinone (0.2 mole %), 5) without inhibitor.

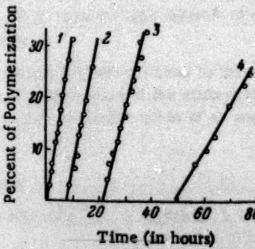


Fig. 2. The kinetics of styrene polymerization in the presence of benzoquinone at 100°.
1) Without inhibitor, 2) benzoquinone (0.1 weight %), 3) the same (0.3 weight %), 4) the same (0.7 weight %).

The results of examining the efficiency of different quinones are given in Fig. 1.

Benzoquinone and naphthoquinone cause a long induction period; the fully substituted quinone, anthraquinone, lacks an inhibiting effect. As will be shown below, this is in accordance with the values of the oxidation-reduction potential of the quinone, which determines its capacity to change into the benzenoid form on reaction with free radicals.

The inhibiting effect of quinones is connected with their reaction with the initial active centers, arising in the thermal activation of styrene. Therefore, as Goldfinger et al. showed [3], the length of the induction period is proportional to the concentration of the inhibitor. In Fig. 2 we present our experimental data confirming this relation.

We should mention that with an increase in the concentration of the quinone, we observed a tendency toward the reduction of the rate of polymerization after the induction period, which was caused by the effect of the products of reaction of quinone with the initial active centers. The length of the induction period is greater, the lower the temperature (Fig. 3).

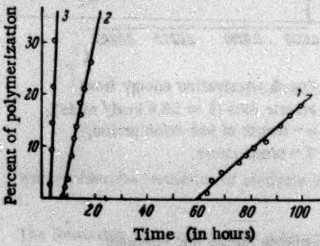


Fig. 3. The kinetics of styrene polymerization in the presence of 0.1 weight % of benzoquinone at 80° (1), 100° (2) and 120°(3).

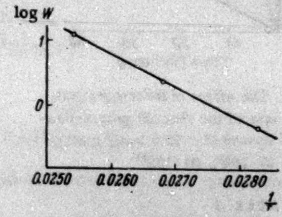


Fig. 4. The activation energy from the values of the induction periods (E — 22.5 kcal/ mole). n — length of the induction period, T — temperature.

At a given concentration of quinone, the following relation must be fulfilled:

$$\frac{n_1}{n_2} = \frac{\alpha_2}{\alpha_1},$$

where $n_1$ and $n_2$ are the lengths of the induction periods at the temperatures $T_1$ and $T_2$ and $\alpha_1$ and $\alpha_2$ are the numbers of initial active centers, arising at the same temperatures during the induction periods $n_1$ and $n_2$.

Substituting the corresponding reciprocal values of the induction periods for the ratio of the rates of formation of the initial active centers in the Arrhenius formula, we can calculate the activation energy of the process. The value of the activation energy, calculated from the values of the induction periods is equal to 22.5 kcal/ mole (Fig. 4).

The activation energy, calculated from kinetic data for the thermal polymerization of styrene (Figs. 5 and 6) equals 22.6 kcal/ mole.

The good agreement between the activation energies calculated from the polymerization kinetics for pure styrene and the values of the induction periods in the presence of benzoquinone at different temperatures indicates that all the active centers formed during the thermal activation of styrene are deactivated during the induction period by reaction with the inhibitor.

The mechanism of benzoquinone inhibition of the thermal polymerization of styrene. During the induction period caused by the presence of quinone, the latter is gradually consumed to form hydroquinone and other products from its reaction with styrene. In Table 1 we give data on the kinetics of the consumption of benzoquinone and the formation of hydroquinone in the thermal polymerization of a 50 % solution of styrene in toluene at 100°.

The data given in the tables show that during the induction period, the benzoquinone is gradually consumed to form a reaction product of styrene and hydroquinone. The yield of hydroquinone reached 35-37 % of the initial benzoquinone at the end of the induction period. It is known that under suitable conditions benzoquinone is a quite strong dehydrogenating agent. The conversion of benzoquinone into the hydroquinone may be the result of its reaction with the polymer (or solvent) or the reaction products formed during the induction period of the polymerization process.

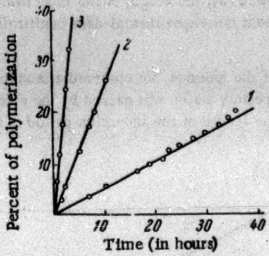


Fig. 5. The effect of the temperature on the rate of the thermal polymerization of styrene (E – 22.6 kcal/ mole). 1) 80°, 2) 100°, 3) 120°.

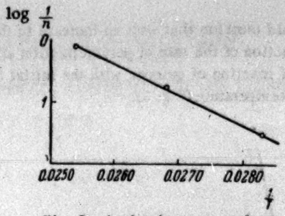


Fig. 6. Activation energy from kinetic data (E = 22.6 kcal/ mole). n – length of induction period, T – temperature.

TABLE 1

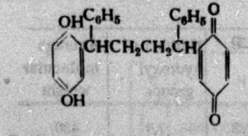
Consumption of Benzoquinone and Formation of Hydroquinone during the Thermal Polymerization of Styrene

| Composition of polymerization mixture | Inhibitor | Inhibitor taken (as % of styrene) | Length of heating at 100° (in hours) | Found (as % of inhibitor introduced) | |
|---|---|---|---|---|---|
| | | | | benzoquinone | hydroquinone |
| 50% solution of styrene in toluene | Benzoquinone | 2.0 | 16 | 56.5, 61.4 | 3.5, 6.1 |
| | | | 20 | 47.1 — | 13.1 — |
| | | | 32 | 27.3, 25.9 | 15.1, 17.0 |
| | | | 47 | 6.3, 5.5 | 35.7, 31.8 |
| | | | 66 | 0.0, 0.0 | 35.7, 36.5 |
| The same | Benzoquinone | 5.0 | 16 | 53.8, 57.1 | 5.7 — |
| | | | 32 | — — | 26.2, 26.0 |
| | | | 47 | 20.7 — | 29.3 — |
| | | | 66 | 0.0, 0.0 | 36.8, 37.0 |
| Pure styrene | Hydroquinone | 1.0 | 1 | 0.0 | 99.2 |
| | | | 5 | 0.0 | 99.9 |
| | | | 144 | 0.0 | 95.2 |

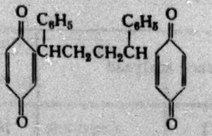
To check the possibility of the benzoquinone dehydrogenating the polymer chain and the solvent, we heated solutions of benzoquinone containing polystyrene and suitable solvents at 100°. 1 % benzoquinone was added to the solutions.

The experimental data obtained are given in Table 2.

The data given in Table 2 show that practically no dehydrogenation of the finished polymer chain or the solvent by the quinone occurs under the conditions of polymerization. From this it follows that the formation of hydroquinone is connected in some way with the act of polymerization inhibition. The product of the reaction of benzoquinone and styrene, which we isolated after heating the latter for a long time with 7-10 % quinone at 100°, was recrystallized several times from benzene to form a light yellow, crystalline substance, which could be separated into two fractions with different melting points by the solubility of benzene: product 1 — 115-130°, product 2 — 185-205°.



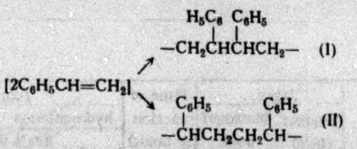
Product 1



Product 2

The presence of 2 molecules of styrene (and not one) in the initial reaction product indicates that the initial active center in the thermal polymerization of styrene is a biradical formed from monomer molecules [5].

The biradical formed in the thermal activation of styrene may have two basic structures



We consider the formation of structure (II) more probable as it corresponds to the most stable form of the radical.

The formation of a considerable amount of hydroquinone (35 - 37 % of the quinone taken) is caused by disproportionation reactions between the products formed.

TABLE 2

| Medium | Time of heating (in hours) | Found (as % of initial benzoquinone) | |
|---|---|---|---|
| | | hydroquinone | benzoquinone |
| 10% solution of polystyrene in ethylbenzene | 0 | 0.0 | 100.4 |
| | 7 | 0.0 | 95.8 |
| | 12 | 0.0 | 94.2, 96.0 |
| | 15 | 0.0 | 97.5, 96.5 |
| Ethylbenzene | 36 | 2.3 | 100 |
| | 78 | 2.3 | 102.5 |
| Isopropylbenzene | 5 | 2.4 | 95.3 |
| | 36 | 2.3 | 95.3 |
| | 78 | 2.3 | 93.0 |

The molecular weight of the products indicated was determined cryoscopically and by Rast's method. The molecular weights of the two fractions of the condensation product of styrene and quinone were identical and equalled 430. The elementary composition of the products is given in Table 3.

The elementary compositions and the molecular weights of the two products were identical. By acetylation it was established that product 1 contained about two (2.3) hydroxyl groups and that hydroxyl groups were absent from product 2. The elementary composition and the molecular weights of the products we isolated corresponded to the compound $C_{28}H_{24}O_4$.

From the oxygen and hydroxyl group contents and the molecular weights, the products we isolated may be preliminarily assigned the structure of the condensate of (product 1) with excess benzoquinone. This was established by running a reaction between product 1 and benzoquinone in ethylbenzene solution at 100° (Table 4).

After cooling, crystals of hydroquinone came down from the mixture. The amount of hydroquinone formed and unreacted quinone was determined by an accepted method [4], as it was established that the presence of condensation products in the mixture did not interfere with this determination.

TABLE 3

| Substance analyzed | Content (in %) |  | Number of hydroxyl groups | Average molecular weight |
|---|---|---|---|---|
|  | C | H |  |  |
| Product 1 | 78.5 | 5.3 | 2.3 | 430 |
| Product 2 | 78.5 | 5.3 | 0.0 | 430 |
| Acetylated condensation product No. 1 | 76.2 | 5.5 | — | 480 |
| Condensation product of 2 molecules of styrene with 2 molecules of quinone (theoretical calculation) | 79.2 | 5.7 |  | 424 |

TABLE 4

| Starting material | Taken |  | Time of reaction (in hours) | Found |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | hydroquinone |  | benzoquinone |  |
|  | product (in g) | benzoquinone (in g) |  | (in g) | (as % of benzoquinone) | (in g) | (as % of initial) |
| Condensation product No. 1 | 0.1000 | 0.0308 | 1 | 0.0145 | 47.1 | 0.0163 | 53.0 |
|  | 0.1953 | 0.0507 | 3 | 0.0425 | 83.8 | 0.0820 | 16.15 |

We should mention that the elementary composition of product 1, after disproportionation with benzoquinone corresponded to the elementary composition of the starting compound and did not contain phenol groups (Table 5).

TABLE 5

| Substance analyzed | Content (in %) |  | Average molecular wt. | Number of hydroxyl groups |
|---|---|---|---|---|
|  | C | H |  |  |
| Product 1, after disproportionation by benzoquinone | 78.0 | 5.7 | 430 | 0.0 |
|  | 78.0 | 5.5 | — | 0.13 |

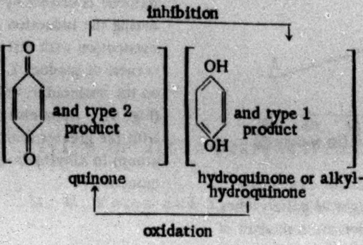
The condensation products of benzoquinone and styrene are inhibitors of the polymerization process and cause (in the absence of oxygen) a long induction period (Fig. 7). As would be expected, product 2, which contains more quinoid groups, shows a stronger inhibiting effect.

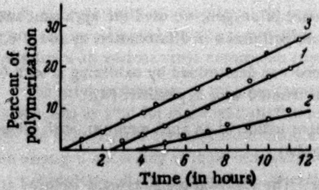
Under actual conditions, i.e. in the presence of oxygen, the inhibiting effect of benzoquinone on the thermal polymerization of styrene, determined by the length of the induction period, considerably exceeds the effect of corresponding amounts of benzoquinone in a nitrogen atmosphere (Fig. 8).

In the absence of oxygen hydroquinone does not cause an induction period. Under the same conditions, the corresponding amount of benzoquinone causes an induction period of 6 hours. Meanwhile, in the presence of benzoquinone or hydroquinone in an atmosphere of air, the polymerization of styrene does not begin after 16 hours.

The experimental data given above permit the following conclusions.

During the induction period, benzoquinone reacts quantitatively with the initial active centers, which is shown by the complete cessation of the polymerization reaction. As a result, condensation products and hydroquinone are formed. The latter is reoxidized to quinone in the presence of oxygen and thus is capable of further reactions with free radicals, which also explains the considerable increase in the induction period in the presence of oxygen.





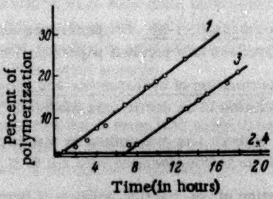


Fig. 7. The effect of condensation products 1 and 2 on the polymerization of styrene in the absence of oxygen.
1) Condensation product 2 (0.099 mole %),
2) condensation product 1 (0.099 mole %),
3) without inhibitor.

Fig. 8. Polymerization of styrene in the presence of hydroquinone and benzoquinone in atmospheres of nitrogen and air.
1) Hydroquinone (0.07 mole %) in nitrogen,
2) the same in air, 3) benzoquinone (0.07 mole %) in nitrogen, 4) the same in air.

The length of the induction period is determined by the length of the "life" of the reversible system. The cycle is broken either after complete consumption of the benzoquinone or after exhaustion of the oxygen, if the reaction is proceeding in a closed system.

TABLE 6

| Name of inhibitor | Concentration ( in mole %) | Molecular weight |
|---|---|---|
| Without inhibitor | — | 290000 |
| Benzoquinone | 0.09 | 256000 |
| Benzoquinone | 1.0 | 87000 |
| Naphthoquinone | 0.47 | 133500 |
| Anthraquinone | 0.47 | 301500 |
| Condensation product 1 | 0.03 | 102000 |
| Hydroquinone | 0.47 | 107600 |

The effect of inhibitors on the molecular weight of polystyrene. In Table 6 we present data on the effect of various quinones, hydroquinone and condensation product 1, containing phenol groups, on the molecular weight of polystyrene.

Anthraquinone does not have any effect on the molecular weight, which agrees with the absence of an inhibiting effect on the polymerization. Benzoquinone and naphthoquinone stop the process at the initial stage and the polymerization process only begins after complete consumption of the quinone. The decrease in the molecular weight of the polymer in the presence of the quinone is caused by the effect of the products formed during the induction period (hydroquinone etc.). In connection with this we must mention the special effectiveness of product 1, which showed a very strong effect on the molecular weight after the induction period (Fig. 9). Apparently, this phenomenon is connected with the greater lability of the hydrogen (in the OH group) in alkylhydroquinones in comparison with hydroquinone.

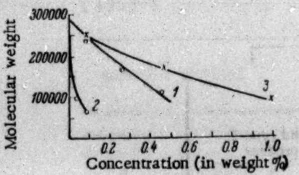


Fig. 9. The effect of inhibitor concentration on the molecular weight of polystyrenes. 1) Hydroquinone, 2) condensation product of styrene and benzoquinone 1, 3) benzoquinone.

## EXPERIMENTAL METHOD

Experimental set-up. For performing experiments in the absence of oxygen, we used the apparatus and method, described in a previous paper [1]. The polymerizations were performed in dilatometers at 100 ± 0.2°.

Determination of hydroquinone and quinone. The hydroquinone was determined by oxidizing it with 0.05 N iodine solution in an acetic acid medium. The excess iodine was titrated with hyposulfite [4].

The quinone was determined by reduction with excess potassium iodide in an acid medium, with subsequent titration of the iodine liberated with a 0.05 N solution of hyposulfite [4].

Isolation of the reaction products of benzoquinone and styrene. The reaction products were isolated after heating styrene with 7-10% of benzoquinone at 100° for 7-10 days. On cooling the solution, a precipitate formed, which was recrystallized several times from benzene to give the condensation products of styrene and benzoquinone. The molecular weights of the given compounds were determined cryoscopically by Rast's method. The molecular weight of polystyrene was determined viscometrically [1].

## SUMMARY

The effect of various quinones on the kinetics of the thermal polymerization of styrene and on the molecular weight of the polymer was studied. The composition of the benzoquinone reaction products formed during inhibition of polymerization was investigated. We examined the problem of the process mechanism on the basis of the results obtained.

## LITERATURE CITED

[1] B. A. Dolgoplosk, D. Sh. Korotkina, J. Gen. Chem. 27, 2226 (1957).*

[2] J. W. Breitenbach, A. Springer and K. Horeischy, Ber. 71, 1438 (1938); S. G. Foord, J. Chem. Soc. 1940, 48-56; J. W. Breitenbach. Handbuch der Katalyse, VII, 333 (1943); W. Kern and K. Feuerstein, J. pr. Ch. 158, 186 (1941); H. W. Melville and W. F. Watson, Trans. Farad. Soc. 44, 886 (1948); Ch. C. Price; Advancing Fronts in Chemistry, I, 37-45 (1945).

[3] G. Goldfinger, J. Skeist and H. Mark, J. Phys. Chem. 47, 578 (1943); F. R. Mayo and R. A. Gregg, J. Am. Chem. Soc. 70, 1284 (1948).

[4] I. Kolthoff, Volumetric Analysis, Vol. 2, State Chem. Tech. Inst. 447 (1932).**

[5] C. Walling, E. R. Briggs and F. R. Mayo, J. Am. Chem. Soc. 68, 1145 (1946).

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** In Russian.

# THE REACTIVITY OF ALLYL DERIVATIVES OF TIN

M. M. Koton and T. M. Kiseleva

Derivatives of tin with various alkyl and aryl radicals have been studied quite thoroughly, but up to the present time tin compounds with a double bond in the hydrocarbon radical have been little investigated. In order to study the reactivity of unsaturated tin compounds we synthesized allyltriphenyltin, diallyldiphenyltin and tetraallyltin and investigated their heat stability, reactions with acids and capacity for polymerization and copolymerization with various vinyl compounds (styrene, methyl methacrylate, vinyl acetate).

The allyl derivatives of tin were found to be heat stable compounds up to 170° and it required long heating (24-48 hours) at 170° for diphenyldiallyltin to undergo partial symmetrization to form heat stable tetraphenyltin, while the tetraallyltin decomposed to form a monoallyl derivative of tin, metallic tin, $SnO_2$ and diallyl. Thus, when arranged according to their heat stability, the allyl derivatives of tin that were studied, form the series: allyltriphenyltin > diallyldiphenyltin > tetraallyltin.

Tetraallyltin reacted vigorously with alcohol solutions of HCl to form propylene and $SnCl_4$ by the equation

$$(C_3H_5)_4Sn + 4HCl \rightarrow 4C_3H_6 + SnCl_4$$

Under the same conditions diallyldiphenyltin gave propylene, benzene, $(C_6H_5)_2SnCl_2$ and $SnCl_4$. Allyltriphenyltin was the most stable and 50 % of it decomposed under these conditions to form benzene, propylene and $SnCl_4$. By treating allyltriphenyltin with iodine in a xylene solution the allyl radical was split out and triphenyltin iodide was formed [1], by the equation

$$C_3H_5Sn(C_6H_5)_3 + I_2 \rightarrow C_3H_5I + (C_6H_5)_3SnI$$

Tetraallyltin reacted vigorously with formic acid at room temperature with the evolution of propylene and the formation of tin tetraformate

$$(C_3H_5)_4Sn + 4HCOOH \rightarrow 4C_3H_6 + (HCOO)_4Sn$$

which, under the experimental conditions, was converted into a basic salt with the composition $(HCOO)Sn(OH)_3$.

Diallyldiphenyltin reacted with formic acid at 50° by the equation

$$(C_3H_5)_2Sn(C_6H_5)_2 + 4HCOOH \rightarrow 2C_3H_6 + 2C_6H_6 + (HCOO)_4Sn$$

Allyltriphenyltin reacted with formic acid only at 90° and decomposed completely to form benzene, propylene and a basic salt $(HCOO)Sn(OH)_3$.

The results obtained agree well with the data obtained earlier by one of the authors [2] when studying the reaction of tetraphenyltin with formic acid, a reaction which started only at 100° and was accompanied by complete decomposition of tetraphenyltin to form benzene and $(HCOO)Sn(OH)_3$. Thus, the allyl derivatives of tin form a series according to their reactivity: tetraallyltin > diallyldiphenyltin > allyltriphenyltin. Consequently, the introduction of an allyl radical into a molecule of an organotin compound raises its reactivity. In reacting with ethyl alcohol at 130°, tetraallyltin decomposed completely to form propylene and stannic hydroxide by the equation

$$(C_3H_5)_4Sn + 4C_2H_5OH \rightarrow 4C_3H_6 + Sn(OC_2H_5)_4$$

$$Sn(OC_2H_5)_4 \xrightarrow{HOH} Sn(OH)_4 + C_2H_5OH$$

We attempted to study the polymerization and copolymerization capacity of allyl derivatives of tin. It was found that the allyl derivatives of tin do not block polymerize in the presence or absence of initiators (the azodinitrile of isobutyric acid).

We then devised experiments to study the effect of the addition of allyl derivatives of tin (5 % by weight) on the polymerization of styrene, methyl methacrylate and vinyl acetate at 120°. In the experiments with styrene, the clear, colorless masses obtained were dissolved in benzene and then precipitated with methanol. After two successive reprecipitations, the styrene polymers were dried to constant weight and we determined their tin content, which was from 0.35 to 4.03 % depending on the nature of the allyl derivatives of tin (Table 1). A considerable slowing down of the polymerization and a fall in polymer yield was observed in the experiments with methyl methacrylate and vinyl acetate. This effect was more noticeable when more allyl groups were in the molecule of the organotin compounds (Table 2).

TABLE 1

The Polymerization of Methyl Methacrylate and Vinyl Acetate in the Presence of Allyl Derivatives of Tin

| Organotin compound | Polymerization time (hours) | Yield of reprecipitated polymer (in %) | Tin content of polymer (in %) |
|---|---|---|---|
| — | 2 | 18.09 | — |
| $(C_3H_5)Sn(C_6H_5)_3$ . | 2 | 17.10 | 0.35 |
| $(C_3H_5)_2Sn(C_6H_5)_2$ | 2 | 18.0 | 0.65 |
| $(C_3H_5)_4Sn$ . . . . | 2 | 19.6 | 0.62 |
| — | 4 | 31.2 | — |
| $(C_3H_5)Sn(C_6H_5)_3$ . | 4 | 28.9 | 0.36 |
| $(C_3H_5)_4Sn$ . . . . | 4 | 21.3 | 4.03 |

TABLE 2

The Polymerization of Methyl Methacrylate and Vinyl Acetate in the Presence of Allyl Derivatives of Tin

| Monomer | Organotin compound | Polymerization time (hours) | Yield of reprecipitated polymer (in %) |
|---|---|---|---|
| Methyl methacrylate | — | 2 | 96.05 |
| | $(C_3H_5)Sn(C_6H_5)_3$ | 2 | 35.80 |
| | $(C_3H_5)_2Sn(C_6H_5)_2$ | 2 | 28.20 |
| | $(C_3H_5)_4Sn$ . . . | 2 | 1.08 |
| | — | 4 | 99.50 |
| | $(C_3H_5)Sn(C_6H_5)_3$ | 4 | 60.90 |
| | $(C_3H_5)_2Sn(C_6H_5)_2$ | 4 | 48.50 |
| | $(C_3H_5)_4Sn$ . . . | 4 | 5.60 |
| Vinyl acetate | $(C_3H_5)_4Sn$ . . . | 2 | 0.90 |
| | $(C_3H_5)_4Sn$ . . . | 4 | 1.02 |

Tetraallyltin was found to be an effective inhibitor of methyl methacrylate and vinyl acetate polymerization. Thus, without tetraallyltin, methyl methacrylate gave, under the experimental conditions, a polymer yield of 96-99 %, and in the presence of 5 % by weight of tetraallyltin the polymer yield decreased under the same conditions to 0.9 - 5.6%. Such a strong inhibiting effect of tetraallyltin was apparently due to its capacity for capturing free radicals. In order to check the accuracy of this hypothesis, we used methylphenyltriazene decomposition in hydrocarbon media [3], which proceeds with the formation of the methane by the equations

$$CH_3{-}N{=}N{-}NH{-}C_6H_5 \rightarrow CH_3\cdot + N_2 + \cdot HNC_6H_5$$

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot$$

In methylphenyltriazene decomposition in α-olefins, the amount of methane falls sharply due to the addition of methyl radicals to the double bond. One could assume that tetraallyltin would also add methyl radicals. For this purpose methylphenyltriazene was decomposed at 100° in a cumene medium with the addition of 0.5 mole % of tetraallyltin and it was shown that the amount of methane in the gas was 25-27 % instead of the usual 50 % of the theoretical. The formation of methane in methylphenyltriazene decomposition could be completely suppressed by increasing the amount of tetraallyltin added.

Thus, it was shown that the strong inhibition of methyl methacrylate and vinyl acetate polymerization by tetraallyltin was closely related to its capacity for reacting with free radicals, formed during the polymerization of vinyl compounds.

## EXPERIMENTAL

Tetraallyltin was prepared from allylmagnesium bromide and $SnCl_4$ in benzene solution [4] in the form of a colorless liquid with b.p. 87-88° (4 mm), $n_D^{32}$ 1.5324 (1.5330 [4]).

Found %: Sn 41.30. $C_{12}H_{20}Sn$. Calculated %: Sn 42.04.

Diallyldiphenyltin was prepared from allylmagnesium bromide and diphenyltin dichloride [5] in the form of a colorless liquid with b.p. 170-173° (5 mm), $n_D^{20}$ 1.6008 (1.6025 [5]). The yield was 48 %.

Found %: Sn 33.9. $C_{18}H_{20}Sn$. Calculated %: Sn 33.43.

Allyltriphenyltin was prepared from allylmagnesium bromide and triphenyltin chloride [5] as crystals with m.p. 73-74° (73-75° [5]). The yield was 62.5 %.

Found %: Sn 30.71. $C_{21}H_{20}Sn$. Calculated %: Sn 30.43.

All the analyses for the tin contents of the organic compounds were by the method of Gilman and Rosenberg [6].

Thermal decomposition of allyl derivatives of tin. On heating 1 g of tetraallyltin in a sealed ampule for 96 hours at up to 170°, no change was observed, but at 170°, decomposition occurred. After heating at 170° for 24 hours, the substance yielded 0.07 g of an infusible, insoluble material, containing 61.06 % tin and corresponding in composition to $CH_2 = CH - CH_2Sn(O)(OH)$ (61.6 % tin). After 48 hours heating at 170°, the tetraallyltin decomposed to form metallic tin, diallyl and $SnO_2$. On heating 0.5 g of tetraallyltin in the presence of 0.1 % of the azodinitrile of isobutyric acid in a sealed ampule and gradually raising the temperature to 160° over a period of 108 hours, the greater part of the tetraallyltin (80 %) remained unchanged and there was also formed 0.05 g of a white, infusible substance containing 55.1 % tin and corresponding in composition to $(CH_2 = CH - CH_2)_2SnO$ (54.8 % tin).

On heating 1 g of diallyldiphenyltin in a sealed ampule at 160° for 96 hours, no change at all was observed, but above 160° (up to 170°) partial symmetrization occurred to form 0.1 g of tetraphenyltin with m.p. 222-224° (found %: Sn 27.2, calculated %: 27.86).

On heating 1 g of allyltriphenyltin in a sealed ampule at 170° for 120 hours there was no change and the substance was recovered unchanged on cooling the ampule.

The reaction of the allyl derivatives of tin with an alcohol solution of HCl. In all the experiments, 0.5 g portions of the allyl derivatives of tin were placed in ampules, which were cooled in a bath of solid carbon dioxide, and then 2 ml of an alcohol solution of HCl was added.

On treating tetraallyltin with an alcohol solution of HCl at room temperature, a vigorous reaction occurred with the voilent evolution of an inflammable gas, which decolorized a solution of $Br_2$ in $CCl_4$. After evaporating off the $CCl_4$, we isolated 1,2-dibromopropane with b.p. 140.1°. Thus it was proved that the gas was propylene. The alcohol solution was diluted with water and neutralized with NaOH; we then observed the quantitative precipitation of stannic hydroxide, which was determined as $SnO_2$ (found 0.25 g $SnO_2$; calculated 0.266 g).

Under the same conditions diallyldiphenyltin reacted with an alcohol solution of HCl to give propylene and benzene; diluting the alcohol solution with water yielded a precipitate (0.09 g – 22 %) of diphenyltin oxide (found %: Sn 39.3. $C_{12}H_{10}SnO$; calculated %: Sn 41.17). After adding NaOH solution, the stannic hydroxide was determined as $SnO_2$ (found 0.1 g, calculated 0.122 g).

Under similar conditions allyltriphenyltin formed propylene, benzene and $SnO_2$ (found 0.08 g, calculated 0.10 g) and left 0.25 g (50 %) of unreacted starting material.

The reaction of allyltriphenyltin with iodine. 0.325 g of iodine was added in small portions to a solution of 0.5 g of allyltriphenyltin in 2 ml of xylene, heated to boiling, and then the liquid was boiled for 4 hours. The xylene was evaporated off and the residue recrystallized from petroleum ether to give crystals of triphenyltin iodide with m.p. 115-117° (117-119° [7]).

Found %: Sn 25.10. $C_{18}H_{15}SnI$. Calculated %: Sn 24.90.

The reaction of the allyl derivatives of tin with formic acid. On adding 0.75 ml of formic acid to 0.5 g of tetraallyltin, a vigorous reaction immediately occurred with the evolution of heat and the liberation of propylene. After working up the reaction mixture, we obtained 0.35 g (calculated 0.38 g) of a white, infusible, insoluble substance, which corresponded in composition to $(HCOO)Sn(OH)_3$.

Found %: Sn 55.6. $CH_4O_5Sn$. Calculated %: Sn 55.35.

On heating 0.5 g of diallyldiphenyltin with 0.75 ml of formic acid in a sealed ampule for 3 hours at 50°, we detected benzene, propylene and 0.26 g (calculated 0.303 g) of $(HCOO)Sn(OH)_3$. On heating 0.5 g of allyltriphenyltin with 0.75 ml of formic acid at 50°, the reaction did not go, but after additional heating for 3 hours at 90°, we observed the evolution of propylene and the formation of benzene and 0.25 g (calculated 0.275 g) of $(CHOO)Sn(OH)_3$.

*The reaction of tetraallyltin with ethyl alcohol.* As a result of heating 0.3 g of tetraallyltin and 3 ml of ethyl alcohol in a sealed ampule for 3 hours at 130°, propylene and 0.15 g (calculated 0.16 g) of $SnO_2$ were formed.

Found %: Sn 61.70. $SnO_2$. Calculated %: Sn 63.30.

*Experiments on the polymerization and copolymerization of allyl derivatives of tin.* The allyl derivatives of tin did not block polymerize on heating to 160° both in the absence of initiators and in the presence of 0.1 % of isobutyric azodinitrile. All the experiments on the copolymerization of allyl derivatives of tin with vinyl monomers (styrene, methyl methacrylate and vinyl acetate) were carried out at 120° for periods of 2 and 4 hours with a ratio of 95 weight % of the monomers to 5 weight % of the tin derivatives. The polymers obtained were dissolved in benzene, precipitated with methanol and dried to constant weight. The results of the experiments are given in Tables 1 and 2.

## SUMMARY

1. It was shown that when arranged according to their heat stability, the allyl derivatives of tin form the series: allyltriphenyltin > diallyldiphenyltin > tetraallyltin.

2. It was shown that in reactions with HCl and formic acid the allyl derivatives of tin may be arranged according to their reactivity in the series: tetraallyltin > diallyldiphenyltin > allyltriphenyltin.

3. Allyl derivatives of tin with aromatic radicals and tetraallyltin do not block polymerize.

4. Tetraallyltin is an effective inhibitor of methyl methacrylate and vinyl acetate polymerization.

## LITERATURE CITED

[1] M. Z. Manulkin, J. Gen. Chem. 13, 42, 47 (1943); J. Gen. Chem. 14, 28, 1047 (1944).

[2] M. M. Koton, J. Gen. Chem. 26, 3212 (1956).*

[3] E. B. Milovskaya, B. A. Dolgoplosk, B. L. Erusalimsky, Bull. Acad. Sci., Div. Chem. Sci. 1957, 494.*

[4] K. Visajaraghava, J. Indian Chem. Soc. 22, 135 (1945); Ch. A. 40, 2787 (1946).

[5] H. Gilman and J. Eisch, J. Org. Ch. 20, 763 (1955).

[6] H. Gilman and D. Rosenberg, J. Am. Chem. Soc. 75, 3592 (1953).

[7] H. Gilman, J. Org. Ch. 18, 1555 (1953).

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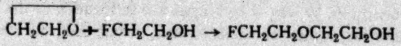
# PRODUCTION OF 2-FLUOROETHYL ETHER OF ETHYLENE GLYCOL

Yu. M. Zinovyev, V. N. Kulokova and L. Z. Soborovsky

The 2-fluoroethyl ether of ethylene glycol was first described by Knunyants, Kildisheva and Petrov [1] by synthesis from ethylene oxide and 2-fluoroethanol.



$$\overline{CH_2CH_2O} + FCH_2CH_2OH \rightarrow FCH_2CH_2OCH_2CH_2OH$$

The reaction was effected under pressure with prolonged heating of the reagents, in the molar ratio of 1 : 3 (54 hrs, 180°, in a steel container).

We have found that the 2-fluoroethyl ether of ethylene glycol is easily obtained by treating 2-fluoroethanol with metallic sodium. Yield of the ether in this case was more than 70%. At the same time, in approximately theoretical amounts, sodium fluoride and gaseous hydrogen were formed. Evidently the reaction proceeds in two stages: at first sodium 2-fluoroethylate is formed, which, with excess 2-fluoroethanol, yields the required ether.

$$2FCH_2CH_2OH + 2Na \rightarrow 2NaOCH_2CH_2F + H_2$$
$$2FCH_2CH_2ONa + 2FCH_2CH_2OH \rightarrow 2FCH_2CH_2OCH_2CH_2OH + 2NaF$$

The reaction described in the present work indicates the relative mobility of the fluorine atoms in the 2-fluoroethanol molecule.

## EXPERIMENTAL

34.71 g of 2-fluoroethanol, prepared according to Hoffman [2], was placed in a distillation flask, and 2 g metallic sodium gradually added. During the reaction the flask was cooled with ice-water. On completion of solution of the sodium the unreacting 2-fluoroethanol (21.4 g) was first distilled off from the reaction mass, and then a substance boiling at 58-62° (7 mm). With a second distillation 7.99 g of substance separated. Yield calculated on the 2-fluoroethanol used was 71.5 %, and, on the metallic sodium, 85.0 %.

B. p. 169-171°, $d_4^{20}$ 1.1216, $n_D^{20}$ 1.4070, $MR_D$ 23.81; calc. 23.81.

Found %: C 44.30, 44.41; H 8.92, 8.77. $C_4H_9O_2F$. Calculated %: C 44.43; H 8.39.

## SUMMARY

1. It has been shown that 2-fluoroethanol, when reacted with metallic sodium, easily forms with good yield, the 2-fluoroethyl ether of ethylene glycol.

2. Unlike the di- and trifluoroethanols, forming relatively stable alcoholates of sodium, it was not possible, with 2-fluoroethanol, to separate a stable alcoholate, because this latter, with excess alcohol, is at once converted into the 2-fluoroethyl ether of ethylene glycol.

## LITERATURE CITED

[1] I. L. Knunyants, O. V. Kildisheva and I. P. Petrov, J. Gen. Chem. 19, 99 (1949).*

[2] F. Hoffman, J. Am. Chem. Soc. 70, 2596 (1948).

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* Original Russian pagination. See C. B. Translation.

# ON THE MECHANISM OF REGROUPING α- INTO β-NAPHTHALENESULFONIC ACID

F. M. Vainshtein and E. A. Shilov

We showed recently that the reversible regrouping of o- and p-toluenesulfonic acids in concentrated sulfuric acid proceeds completely, or nearly so, by way of hydrolysis and sulfonation of the toluene formed, and not as an intramolecular process [1]. However, it must be admitted that, in this case, the stereochemical conditions are not favorable for intramolecular displacement of the sulfo groups (meta-migration). Such steric hindrances do not exist in the displacement of the sulfo groups towards the neighboring atom of carbon (ortho migration). The intramolecular method of transposing the sulfo group becomes more probable in the ortho migration.

The regrouping of α- into β-naphthalenesulfonic acid presents such a case. For this reaction results have been obtained that indicate the role of hydrolysis in its mechanism [2-5]. More especially it is known that α-naphthalenesulfonic acid, in dilute sulfuric acid, undergoes hydrolysis, forming the equilibirum system:

$$\alpha\text{-}C_{10}H_7SO_3H + H_2O \rightleftarrows C_{10}H_2 + H_2SO_4.$$

With sufficiently high concentrations of sulfuric acid, the α-naphthalenesulfonic acid is in equilibrium with the β-isomer. The rate of conversion, as also the rate of sulfonation of naphthalene, increases with increased acidity of the sulfuric acid medium. From this it follows that the regrouping of α-naphthalenesulfonic acid into the β-isomer may proceed by way of hydrolysis.

This, however, does not mean that transposition of the sulfo group in an intramolecular manner may not to some extent occur.

In order to establish whether, besides hydrolytic, there is also intramolecular regrouping, we used the isotopic method with radioactive $S^{35}$ approximately in the same form as in studying the regrouping of o- into p-toluenesulfonic acid [1].

When our work was already well advanced we became aware that the same problem was also the subject of research by a team of Moscow chemists [6]. These authors also used $S^{35}$ as a marked atom, but their method of procedure differed from ours. They did not separate α- and β-naphthalenesulfonic acids, but determined their relative amounts spectrometrically through ultraviolet absorption. Sulfuric acid was previously separated by means of paper chromatography. It was found that, on heating α-naphthalenesulfonic acid up to 160° in glycerine, neither hydrolysis nor regrouping took place; in a medium of 85% $H_3PO_4$ there was hydrolysis of the sulfo acid, but the β-isomer was not formed. In concentrated sulfuric acid, interchange with the medium takes place to a markedly less degree than the regrouping of α-sulfo acid into the β-isomer. Observations relative to the sulfuric acid medium were not explained. With reference to the experimental results in glycerine and phosphoric acid media, the authors are inclined to doubt the possibility of intramolecular regrouping. Yet it must be pointed out that the absence of any reaction in glycerine is easily explained by the very considerable lowering of acidity through formation of oxonium compounds; and as for the phosphoric acid medium, here again, acidity may be inadequate for intramolecular migration of the sulfo groups.

In view of these considerations, our results with the regrouping of α-naphthalenesulfonic acid, in a concentrated sulfuric acid medium should be of interest.

## EXPERIMENTAL

Materials: We prepared α-naphthalenesulfonic acid by sulfonating naphthalene with the monohydrate at a temperature not exceeding 20° [7]. The aqueous solution of the mixture was separated from the naphthalene and the aqueous suspension treated with lead carbonate. The α-naphthalenesulfonic acid remained in solution as the lead salt, while the β-isomer and sulfuric acid passed down into the precipitate. (It is interesting to note that, by this method, we can take advantage not only of the lower solubility of the β-isomer lead salt [8] but also of its low rate of solution [9] even at a boiling temperature). After the precipitate had been separated, hydrogen sulfide was passed into the filtrate. The PbS was filtered off, and treatment of the filtrate with lead carbonate and hydrogen sulfide was twice repeated. Then the aqueous solution of α-naphthalenesulfonic acid was evaporated in vacuum at 50-60° to a syrupy consistency. The sulfo acid in this case is not hydrolyzed (negative reaction with $BaCl_2$). The α-naphthalenesulfonic acid was settled out from the syrup with 30 % hydrochloric acid, and this operation was repeated several times. The product obtained, α-naphthalenesulfonic acid, dried in a vacuum desiccator over solid caustic soda, showed on analysis the composition $C_{10}H_7SO_3H \cdot 2H_2O$. The absence of the β-isomer was indicated by analytical reactions with phenylhydrazine, benzidine hydrochloride, and ferric chloride [10].

We obtained β-naphthalenesulfonic acid by Witt's method [11], by sulfonating the naphthalene with sulfuric acid (d 1.84) for 20 minutes at 160°. It was thrice precipitated from an aqueous solution of concentrated hydrochloric acid. Tests for the α-isomer with the aid of m-nitro-o-anisidine did not reveal its presence. The composition of the sulfo acid, dried over caustic soda, was found by analysis to be $C_{10}H_7SO_3H \cdot 3H_2O$.

Separation of the isomers. In the mixture after reaction α- and β-naphthalenesulfonic acids, sulfuric acid, naphthalene, and probably some side-products were present. Treatment of the mixture was designed to separate β-naphthalenesulfonic acid free from the α-isomer.

We first thought of using the known methods of separating the α- and β-isomers of the sulfo acids, as used in analyzing sulfonated mixtures [2a, 12, 13], but control experiments in separating mixtures of radioactive α-naphthalenesulfonic acid and the inactive β-sulfo acid (2 : 1) showed that these methods were not suitable for our purpose. We also used the method of precipitating β-sulfo acid with the aid of phenylhydrazine [12] and benzidine [13]; but after careful washing of the precipitates the residual salts of the β-sulfo acid were strongly radioactive, i.e. they contained a high percentage of the α-isomer (11-15 %). Separation by means of lead, barium, or calcium salts from aqueous or aqueous-alcoholic solutions gave similar or even worse results. We also tried a method such as the three-stage. From the mixture of α- and β-sulfo acids the calcium salt of the β-sulfo acid first separated out; then the α-naphthalenesulfonic acid in the form of its difficultly soluble salt, together with m-nitro-o-anisidine [12], separated; and finally, the β-isomer was precipitated from the filtrate as the phenylhydrazine salt. It was found, after these three precipitations, that the β-sulfo acid obtained still contained, judging from its measured radioactivity, about 7 % of the α-isomer.[*]

We found finally that a satisfactory method of freeing the β-sulfo acid from the α-isomer was that of acid hydrolysis of the mixture. As is known, α-naphthalenesulfonic acid is hydrolyzed much more easily in an acid medium than is the β-isomer [9, 5]. In selecting suitable conditions of reaction we developed the following mode of procedure that permitted hydrolyzing the whole of the α-isomer, while preserving the greater part of the β-naphthalenesulfonic acid.

After reaction, 3 volumes of 33% hydrochloric acid were added to the mixture which weighed about 1 g and consisted of α- and β-naphthalenesulfonic acids together with sulfuric acid. This mixture was heated in a sealed ampoule for 1 hour at 180-182° (requiring some care as the vessel may sometimes burst). The contents were treated with water until complete solution of the β-sulfo acid, and the naphthalene filtered off. Hydrogen chloride was removed from the filtrate by passing through an inert gas at 100°.

Control tests showed that, by this method of hydrolysis, the dinaphthalenesulfonic acid is not formed in addition to the β-sulfo acid.

The β-sulfo salt obtained in this way contains from 0 to 0.5% radioactive α-naphthalenesulfonic acid.

Further treatment of the mixture obtained consisted in conversion of the β-sulfo acid into the barium salt and separation from sulfuric acid. The salt was recrystallized from water, washed with cold water, and dried. The specific radioactivity of the product obtained was determined by the usual method, described in detail in [1]. In order to obviate the need of correction for self-absorption by the sulfo salt, a sufficiently small portion (1-2.5 mg) of the barium salt in the form of a fine suspension in methyl alcohol was applied to a plate. Impulse readings were taken on a B instrument with end recorder. From each precipitate test samples were selected for several measurements, and in each sample the radioactivity was measured several times with different positions of the plate. The mean error was evaluated as within ± 5%. Specific activity was expressed in impulses • $mg^{-1}$ • $min^{-1}$.

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[*] On analyzing the naphthalene sulfo-mixtures the methods used by us give, as is known, satisfactory results. This can probably be explained through the compensation of losses of the β-sulfo acid by admixture of adsorbed α-isomer.

Experimental work and results. Mixtures of α-naphthalenesulfonic acid with sulfuric acid were put into ampoules of 10 ml capacity. Taking into account the water of crystallization content, the quantity and concentration of sulfuric acid were so chosen that 81 or 91 % of this acid was present in the mixture. Higher concentrations were avoided on account of the risk of formation of the disulfo acids. The ampoules were sealed and placed in an aluminum block that was heated up to 150 or 160° (± 2°), and held for some time at that temperature. The ampoules were then removed from the block and their contents analyzed.

A small part of the mixture was dissolved in water and treated with barium carbonate. The filtrate containing the barium salts of α- and β-sulfo acids was evaporated to dryness, and the specific radioactivity in the residue was measured. The greater part of the mixture was transferred to another ampoule for sealing, and after addition of concentrated hydrochloric acid it was subjected to hydrolysis and subsequent operations as described above.

In view of the fact that β-naphthalenesulfonic acid, under the conditions of regrouping, gradually exchanges the sulfo group with sulfuric acid, the found percentage of intermolecular hydrolytic regrouping may appear greater than is actually the case. In order to apply the appropriate check we measured in parallel tests the exchange of β-naphthalenesulfonic acid with sulfuric acid under all the conditions of the main experiment. Taking into account that the rate of exchange, as determined in the control tests, is retained in the regrouping of the α-sulfo acid, we added to the found percentage of the direct regrouping (a) a value $a \cdot b/100$, where b is the percent exchange of β-naphthalenesulfonic acid obtained from the parallel test. This check is only approximate and provisional; but there are apparently no data available on which to base a better approximation.

The experimental results, in which the mixture comprised nonradioactive α-naphthalenesulfonic acid and radioactive sulfuric acid, are given in Table 1. Supplementary Table 1a gives the results of the parallel determinations of exchange for β-naphthalenesulfonic acid.

The data in Table 1 shows that the activity of the separated β-isomer is always less than that calculated for complete exchange with radioactive sulfuric acid. The reaction proceeds quickly, as a result of which the values of specific radioactivity of summated α- and β-isomers differ little from that of β-naphthalenesulfonic acid. With extended heating time exchange increases, evidently through gradual exchange of the formed β-sulfo acid with sulfuric acid. Mixing or stirring does not produce any appreciable effect (ampoules 2 and 2a). The values of the percentage intramolecular regrouping in the whole run, with adjustment for exchange of the β-sulfo acid, are given in the last column of Table 1. On an average, this percentage is about 30.

In another series of experiments the mixtures consisted of highly active α-naphthalenesulfonic acid and nonradioactive sulfuric acid. In these experiments it was possible to increase considerably the ratio of quantities of sulfuric acid and α-sulfo acid. After the reaction we determined the radioactivity of the total of the α- and β-isomers, of the pure β-isomer, and of sulfuric acid (as $BaSO_4$).

The results are given in Table 2, and the results of parallel tests for exchange of β-naphthalenesulfonic acid in Table 2a.

It can be seen that the activity of the β-isomer is much greater than it would be if there was complete exchange with the medium. Changes in the ratio $H_2SO_4$/α-sulfo acid within the limits of 3 : 1 and 30 : 1 do not alter the percentage of direct reaction. On an average, about 20 % of the α-naphthalenesulfonic acid is regrouped without interchange with the medium.

Thus, there remains no doubt that in a medium of concentrated sulfuric acid, part of the $SO_3H$ group migrates from the α- to the β-position without previous mixing with molecules of the solvent.

The mechanism of such migration could be represented in a scheme where the role of proton-donor in the reaction complex is taken into account:

TABLE 1

Regrouping of Nonradioactive α-Naphthalenesulfonic Acid in Presence of Radioactive Sulfuric Acid.

| Expt. No. | Experimental conditions | Ampoule No. | Comp. of mixture (in g) |  | Heating time (in min) | Spec. activity of α+β-isomers | Sp. activity of β-isomer[*] |  | % intramolecular regrouping |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | α-acid | $H_2SO_4$ |  |  | found | equilibrium | without calc. exchange of β-isomer with $H_2SO_4$ | Incl. exchange of β-isomer |
| 1 | 150°, initial $H_2SO_4$ 89% (in expt. 81%), spec. activity 1640[*] | 1 | 0.873 | 1.309 | 10 | 265 | 301 | 423 | 29 |  |
|  |  | 2 | 0.621 | 0.931 | 20 | 304 | 308 | 422 |  |  |
|  |  | 2a[**] | 0.616 | 0.924 | 20 | 305 | 308 | 425 |  |  |
|  |  | 3 | 0.499 | 0.698 | 40 | 344 | 334 | 414 | 20 | 28 |
|  |  | 4 | 0.267 | 0.400 | 130 | 383 | 352 | 424 | 18 | 27 |
|  |  | 5 | 0.199 | 0.298 | 280 | 410 | 413 | 424 |  |  |
| 2 | 150°, initial $H_2SO_4$ 89% (in expt. 81%) spec. activity 1563 | 1 | 0.416 | 0.622 | 10 | 271 | 289 | 405 | 29 | 32 |
|  |  | 2 | 0.329 | 0.494 | 45 | 333 | 313 | 405 | 24 | 33 |
| 3 | 150°, initial $H_2SO_4$ 98% (in expt. 91%), spec. activity 1744 (for ampoule 1848) | 1 | 0.369 | 0.554 | 10 | 377 | 372 | 483 | 23 | 28 |
|  |  | 2 | 0.331 | 0.496 | 30 | 390 | 376 | 464 | 19 | — |
|  |  | 3 | 0.285 | 0.428 | 50 | 400 | 379 | 461 | 18 | 30 |
|  |  | 4 | 0.269 | 0.403 | 90 | 418 | 411 | 454 | 9 | — |
| 4 | 160°, initial $H_2SO_4$ 98% (in expt. 91%) spec. activity 1510 | 1 | 0.385 | 0.578 | 10 | 261 | 268 | 395 | 32 | 42 |

TABLE 1a

Exchange Between Nonradioactive β-Naphthalenesulfonic Acid and Radioactive Sulfuric Acid

| Expt. No. | Experimental conditions | Ampoule No. | Comp. of mixture (in g) |  | Heating time (in min) | Spec. activity of α+β-isomers |  | Percent exchange "b" |
|---|---|---|---|---|---|---|---|---|
|  |  |  | α-acid | $H_2SO_4$ |  | found | equilibrium |  |
| 1a—2a | 150°, initial $H_2SO_4$ 89% (in expt. 81%), spec. activity 1720 | 1 | 0.250 | 0.411 | 10 | 53 | 461 | 13 |
|  |  | 2 | 0.250 | 0.410 | 50 | 182 | 461 | 39 |
|  |  | 3 | 0.240 | 0.411 | 120 | 242 | 461 | 52 |
| 3a | 150°, initial $H_2SO_4$ 98% (in expt. 91%) spec. activity 1744 | 1 | 0.225 | 0.381 | 10 | 107 | 476 | 23 |
|  |  | 2 | 0.170 | 0.280 | 50 | 299 | 447 | 66 |
| 4a | 160°, initial $H_2SO_4$ 98% (in expt. 91%), spec. activity 1510 | 1 | 0.366 | 0.605 | 10 | 124 | 418 | 30 |

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[*] Specific activity is expressed as impulses $\cdot$ mg$^{-1}$ $\cdot$ min.$^{-1}$.

[**] Expt. 1-2a was done with shaken up ampoule.

TABLE 2

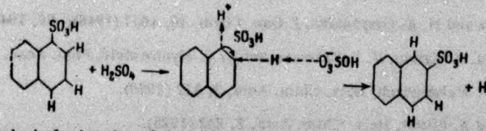
Regrouping of Radioactive α-Naphthalenesulfonic Acid in the Presence of a Nonradioactive Medium

| Expt. | Experimental conditions | Ampoule No. | Comp. of mixture (in g) | | Ratio of α-acid to $H_2SO_4$ | Heating period (in min) | Specific activity of α + β isomers | Specific activity $H_2SO_4$ | | Spec. activity β-isomer | | Percent intramolecular regrouping | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | α-acid | $H_2SO_4$ | | | | found | equilibrium | found | equilibrium | Excluding exchange of β-isomer with $H_2SO_4$ | Including exchange of β-isomer with $H_2SO_4$ |
| 1 | 160°, $H_2SO_4$ 91%, spec. activity — 1700 | 1 | 0.302 | 10.16 | 1 : 30 | 10 | 205 | 42 | 51 | 187 | 17 | 13 | 20 |
| 2 | 150°, $H_2SO_4$ 92%, spec. activity — 1793 | 2 | 0.252 | 2.59 | 1 : 10 | 10 | 237 | 165 | 178 | 244 | 58 | 12 | 18 |
| 3 | 160°, $H_2SO_4$ 91%, spec. activity — 1560 | 1 | 0.252 | 0.80 | 1 : 3 | 10 | 340 | 428 | 468 | 330 | 157 | 14 | 20 |

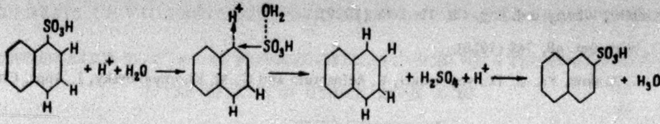
TABLE 2a

Exchange between Nonradioactive β-Naphthalenesulfonic Acid and Radioactive Sulfuric Acid

| Expt. | Experimental conditions | Ampoule No. | Composition of mixture (in g) | | Ratio of β-acid to $H_2SO_4$ | Heating period (in min) | Specific activity | | Percentage exchange "b" |
|---|---|---|---|---|---|---|---|---|---|
| | | | β-acid | $H_2SO_4$ | | | found | equilibrium | |
| 1a | 160°. $H_2SO_4$ 92%, spec. activity – 534 | 1 | 0.204 | 5.82 | 1 : 30 | 10 | 118 | 179 | 65 |
| 2a | 150°, $H_2SO_4$ 91%, spec. activity – 533 | 1 | 0.251 | 2.58 | 1 : 10 | 10 | 90 | 180 | 50 |
| 3a | 160°, $H_2SO_4$ 91.5%, spec. activity – 675 | 1 | 0.102 | 0.29 | 1 : 3 | 10 | 80 | 200 | 40 |



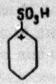
The hydrolytic method of migration of the sulfo groups may be said to compete with this reaction



But it would be possible also to suppose that the reaction proceeds wholly by way of the hydrolysis scheme, yet the separating complex $SO_3H^+ \leftarrow OH_2$ or $SO_3H^+OSO_3H^-$ at once reacts with a molecule of naphthalene at the β position, being unable to mix with solvent molecules ("cell" effect).

The isotope method does not allow a choice to be made between these alternatives.

It should be noted that the regrouping of α-naphthalenesulfonic acid into the β-isomer is not very advantageous for observing intramolecular migration, in view of the fact that α-isomer is much more easily hydrolyzed than isomerized (by sulfonation or direct transposition of the sulfo group).



(I)

Experiments in the migration of sulfo groups would probably be more informative with those compounds where the chances of one or the other reaction would be about equal. Such a case might be found in benzenesulfonic acid marked with the carbon atom $C^{14}$ (I). By studying the structure of the reaction products and determining the extent of change in radioactivity of the sulfo group, it should be possible to establish the degree and direction of migration of the sulfo group. In the case of an intramolecular reaction scheme one would have to expect evidently a much greater development of the reaction without exchange than is the case with regrouping of α-naphthalenesulfonic acid into the β-isomer.

## SUMMARY

With the aid of radioactive sulfur $S^{35}$ it was established that the regrouping of α- into β-naphthalenesulfonic in concentrated sulfuric acid reaches 70-80 % by exchange with the medium, and 30-20 % without.

Regrouping with exchange comprises the stages of hydrolysis of the sulfo acids and sulfonation of the naphthalene formed.

For the regrouping without exchange two explanations are proposed: either this is an intramolecular regrouping, or it is the result of insufficiently rapid diffusion of the complex consisting of the separated sulfo group and its acceptor.

It was found that different analytical methods of determining β-naphthalenesulfonic acid in mixtures with the α-isomer cannot be used for accurate separation of the isomers, since the precipitates obtained of inorganic and organic salts of β-naphthalenesulfonic acid always contain an admixture of the α-isomer.

## LITERATURE CITED

[1] E. A. Shilov and F. M. Vainshtein, Ukr. Chem. J. 21, 58 (1955).

[2] N. N. Vorozhtsov, Fundamentals in the Synthesis of Intermediates and Dyes, Moscow, State Chem. Press, pp 70-78 (1955); (a) p 103.*

[3] Ch. Suter. The Organic Chemistry of Sulfur, London, 268, 390 (1944); I. S. Ioffe, Sulfonation of Organic Substances, Leningrad, Pub. Military Medical Acad. 217 (1944).*

[4] A. A. Spryskov, J. Gen. Chem. 16, 2126 (1946); 17, 591, 1309 (1947); Collected Works, II, 882 (1953).

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* In Russian.

[5] A. A. Spryskov and N. A. Ovsyankina, J. Gen. Chem. 16, 1057 (1946); 20, 1043 (1950);* 21, 1508 (1951).*

[6] S. E. Shnol, Ya. K. Syrkin, V. I. Yakerson and A. A. Blyumenfeld, Proc. Acad. Sci. USSR 101, 1075 (1955).*

[7] H. Fierz and P. Weissenbach, Helv. Chim. Acta, 3, 312 (1920).

[8] F. Ephraim and A. Pfister, Helv. Chim. Acta, 8, 232 (1925).

[9] V. Merz and W. Weith, Ber. 3, 195 (1870).

[10] Ambler, Wherry Ind. Eng. Ch. 12, 1086 (1920).

[11] O. Witt, Ber. 48, 743 (1915).

[12] Z. E. Zinkov, Ya. A. Danyushevskii, V. Reinshtein and G. M. Khomyakovsky, J. Appl. Chem. 9, 1997 (1939).

[13] A. Chuksanova and I. Bilik, Aniline Dye Ind. 3, 459 (1933).

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* Original Russian pagination. See C.B. Translation.

# THE SYNTHESIS OF THIAZOLIDONE DERIVATIVES OF BIOLOGICAL INTEREST

## V. THE CONDENSATION REACTION OF MONOCHLOROACETIC ACID WITH THIOSEMICARBAZONES IN THE PRESENCE OF HYDROCHLORIC ACID

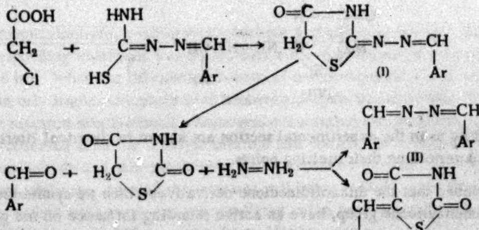
N. M. Turkevich and E. V. Vladzimirskaya

In previous communications [1-3] we showed that when monochloroacetic acid is condensed with thiosemicarbazones derivatives of thiazolidine-2,4-dione-2-hydrazone are formed. In similar condensation reactions carried out by Chabrier [4] and also by Buu-Hoi and his co-workers [5] ethyl alcohol was used as the solvent. We used glacial acetic acid as both solvent and condensing medium; this made it possible to introduce aldehyde groups into the molecules of the condensation products and, therefore, to obtain 5-arylidene derivatives of thiazolidine-2,4-dione-2-hydrazone in one stage.

One of us suggested [6] the use of concentrated hydrochloric acid as the condensing medium for the condensation of monochloroacetic acid with thiourea and this made it possible to obtain high yields of thiazolidine-2,4-dione and its derivatives. The object of the present work was to conduct similar investigations on the thiosemicarbazones of aromatic aldehydes which, as is known, may be considered as derivatives of thiourea.

To carry out these investigations the thiosemicarbazones of benzaldehyde, anisaldehyde, p-acetamino-, m-nitro- and o-chlorobenzaldehydes and salicylaldehyde wereboiled with monochloroacetic and concentrated hydrochloric acids for 1-6 hrs. The condensation products were precipitated by water from the mixtures obtained and were crystallized.

The results of the investigations showed that the reaction products were mixtures of 5-arylidenethiazolidine-2,4-diones (III) and diarylideneazines (II). The reaction mechanism may be represented [7, 8] by the following system:

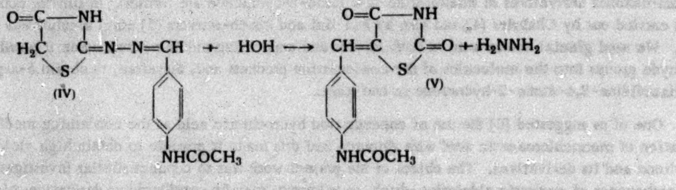


The intermediate reaction products were thiazolidine-2,4-dione-arylidene-2-hydrazones (I) which, like all pseudo-thiohydantoin derivatives, are hydrolyzed by hydrochloric acid with the formation of thiazolidine-2,4-dione. By-products of the reaction were aromatic aldehyde ArCHO and hydrazine which by reacting with each other were converted into diarylidene azines (II). A condensation reaction between the aldehyde and thiazolidine-2,4-dione took place simultaneously, as a result of which 5-arylidene derivatives of the latter (III) were formed.

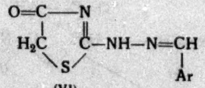
We encountered certain difficulties in the separation and purification of the components of the condensation product. For example, when the thiosemicarbazones of m-nitro- and o-chlorobenzaldehyde and salicylaldehyde were used in the reaction investigated by us azines were the only substances we succeeded in isolating from the condensation products in the pure form. When the thiosemicarbazones of benzaldehyde and anisaldehyde were used we isolated the 5-benzylidene- and 5-anisylidene derivatives, respectively, of thiazolidine-2,4-dione from the condensation product. To the best of our knowledge the 5-anisylidene derivative has not been described hitherto in chemical literature.

In the case of thibone we found thatsaponification of the acetyl group by hydrochloric acid occurred at the same time and the final reaction product was, therefore, not 5-p-acetaminobenzylidenethiazolidine-2,4-dione (V) but the 5-p-aminobenzylidene derivative.

To obtain additional proofs of the correctness of our proposed system we made it our aim to carry out the acid hydrolysis of the intermediate products (I). For this purpose the p-acetaminobenzylidenehydrazone of thiazolidinedione (IV), the synthesis of which we have previously described [2], was boiled for 3 hrs with concentrated hydrochloric acid. The reaction product was in fact found to be 5-p-acetaminobenzylidenethiazolidine-2,4-dione (V). Its formation may be represented by the following system:



The formation of the latter substance proves not only the correctness of our proposed system but also the correctness of the thiazolidone structure of the condensation products of thiosemicarbazones and monochloroacetic acid. It must be mentioned that in their numerous works both Chabrier and Buu-Hoi assume structure (VI), i. e., that of 2-arylidenehydrazothiazoline-4-ones, for similar condensation products. The possibility of the conversion of these latter compounds into thiazolidene-2,4-dione with good yields is, however, not very probable. In addition, as we have shown [9], the absorption spectra of the initial products (I) and also their specific acidic properties exclude the possibility of assuming a thiazolinone structure (VI).



(VI)

The azines described by us in the experimental section are known in chemical literature and were, therefore, identified by merely determining their melting points.

It must also be mentioned that the thiazolidinedione derivatives which we synthesized, containing an aminobenzylidene and acetaminobenzylidene group, have an active retarding influence on the growth of tubercular bacilli.

## EXPERIMENTAL

5-Benzylidenethiazolidine-2,4-dione (III; Ar = $C_6H_5$). 1.6 g of benzaldehyde thiosemicarbazone was boiled with 1.9 g of monochloroacetic acid in 20 ml of conc. HCl for 2 hrs with a reflux condenser. When the transparent solution, initially formed, had been boiled for 10 min a yellow precipitate began to be deposited. After the mixture had cooled it was diluted with water, the precipitate was filtered, washed with water and dried in air. 0.3 g (yield 15.7%) of a yellow crystalline substance was obtained. The m. p. was 237-239° (from alcohol); this corresponds to the data in literature [10] for benzylidenethiazolidinedione.

**5-Anisylidenethiazolidine-2,4-dione (III; Ar = p-$CH_3OC_6H_4$).** 2.1 g of the thiosemicarbazone of anisaldehyde was boiled with 2.5 g of monochloroacetic acid in 40 ml of conc. HCl with a reflux condenser. After the transparent solution had been boiled for 10 min the formation of an oil, which was evidently anisaldehyde, was observed. A further 10 ml of conc. HCl was added to the mixture and boiling was continued for 6 hrs. The reaction product was diluted with an equal volume of water and was then boiled for a further 2 hrs. The boiling mixture was filtered and the residue washed with water and dried. 0.7 g of a light-yellow crystalline substance (yield 30%) with an m. p. of 212-213° (from alcohol) was obtained. The compound was soluble in acetone and pyridine in the cold and in benzene, chloroform, glycerol, alcohol, acetic acid and aqueous solutions of NaOH with heating.

Found %: N 6.03. $C_{11}H_9O_3NS$. Calculated %: N 5.95.

After the 5-anisylidenethiazolidine-2,4-dione had been separated from the hydrochloric acid filtrate a precipitate was deposited from the latter when cooled; this precipitate was again filtered, washed with an aqueous solution of sodium acetate and then recrystallized from alcohol. 0.7 g of a yellow substance (yield 52%) was obtained. The m. p. was 168° (completely transparent liquid at 173°), corresponding to anisaldazine (II; Ar = p-$CH_3OC_6H_4$ [11]).

**5-p-Aminobenzylidenethiazolidine-2,4-dione (III; Ar = p-$NH_2C_6H_4$).** 11.8 g of thibone was boiled with 6.0 g of monochloroacetic acid in 50 ml of conc. HCl with a reflux condenser for 1 hr. A red-orange precipitate was deposited after the transparent solution formed had been boiled for 30 min. During the process of cooling the reaction mixture was diluted with a conc. aqueous solution of sodium acetate. The precipitate was filtered, washed with water and dried in air. 9.8 g of a dark-red substance (yield 89%) with a m. p. of 235° (from alcohol, with decomp.) was obtained.

Found %: N 12.66. $C_{10}H_8O_2N_2S$. Calculated %: N 12.72.

**5-p-Acetaminobenzylidenethiazolidine-2,4-dione (V).** 5 g of thiazolidine-2,4-dione-p-acetaminobenzylidene-2-hydrazone (IV) was boiled with 50 ml of conc. HCl for 3 hrs with a reflux condenser. The transparent yellow-orange solution which was initially formed turned gradually dark-red and after it had been boiled for 20 min a dark-red precipitate was formed. After the solution had cooled the precipitate was filtered, washed with water and dried in air. 1.8 g (38%) of a product, which had an orange color after crystallizing from alcohol, was obtained. The m. p. was 257° (with decomp.) which corresponds to literature data [12] for p-acetaminobenzylidenethiazolidinedione.

Found %: N 10.94. $C_{12}H_{10}O_3N_2S$. Calculated %: N 10.68.

**Azines of m-nitrobenzaldehyde, o-chlorobenzaldehyde and salicylaldehyde.** 100 mmoles of the thiosemicarbazones of the corresponding aldehydes was boiled with a 2.5-fold excess of monochloroacetic acid and 20-60 cc of conc. HCl for 2-6 hrs. When the thiosemicarbazone of o-chlorobenzaldehyde was introduced into the reaction the formation of an oily liquid, evidently o-chlorobenzaldehyde was observed. In this instance alcohol was, therefore, added to the reaction mixture until a homogeneous solution was obtained. Precipitation of the o-chlorobenzaldazine was only observed after the reaction mixture had cooled. In contrast to this, when the thiosemicarbazones of m-nitrobenzaldehyde and salicylaldehyde were introduced into the reaction precipitation of the corresponding azines occurred while the reaction mixture was still being boiled. After the latter had cooled the precipitates were filtered, washed with water and recrystallized twice from glacial acetic acid. m-Nitrobenzaldazine with a m. p. of 196° [11] (yield 82%), o-chlorobenzaldazine with a m. p. of 147° [13] (yield 90.3%) and salazine with a m. p. of 215° [11] (yield 54%) were obtained.

## SUMMARY

1. When the thiosemicarbazones of aromatic aldehydes are condensed with monochloroacetic acid in the presence of concentrated hydrochloric acid 5-arylidene derivatives of thiazolidinedione and the azines of the corresponding aldehydes are formed.

2. As a result of the acid hydrolysis of thiazolidine-2,4-dione-arylidene-2-hydrazones a characteristic migration of the arylidene group into the 5-position and the formation of 5-arylidenethiazolidine-2,4-diones occur.

## LITERATURE CITED

[1] N. M. Turkevich and E. V. Vladzimirskaya, J. Gen. Chem. 24, 2010 (1954).*

[2] E. V. Vladzimirskaya and N. M. Turkevich, J. Gen. Chem. 25, 2150 (1955).*

[3] E. V. Vladzimirskaya, J. Gen. Chem. 27, 1345 (1957).*

[4] P. Chabrier, Bull. Soc. Chim. (5) 14, 797 (1945).

[5] Ng. Ph. Buu-Hoi, Ng. D. Xuong, R. Royer, and D. Lavite, J. Chem. Soc. 1953, 547.

[6] E. V. Vladzimirskaya, J. Gen. Chem. 25, 2255 (1955).*

[7] E. V. Vladzimirskaya, Scientific Works on the Problem: "Synthesis and Investigation of Medicinal Substances" [In Russian] (1956), p. 6.

[8] E. V. Vladzimirskaya, Abstract of Author's Thesis, Lvov (1956).

[9] N. M. Turkevich and E. V. Vladzimirskaya, J. Gen. Chem. 27, 1348 (1957).*

[10] R. Andreasch, Monatsh. 10, 73 (1889).

[11] N. Schapiro, Ber. 66, 1103 (1933).

[12] G. Taniyama and S. Takemura, Yakugaku Dzhassi 73, 164 (1953); Referat Zhur. Khim., 1954, 35867.

[13] T. Curtius and H. Pauli, Ber. 34, 847 (1901).

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# THE PROBLEM OF THE REACTION OF KETENE WITH NITROGEN-CONTAINING BASES

## IV. THE ACETYLATION OF THE ALKALOIDS OF ANABASIS BY KETENE

Yu. V. Svetkin

The reaction of ketene with alkaloids has hitherto hardly been studied. Works which are available in this field are of a specific character and no laws governing this reaction have been found yet. Among investigations of this type we may mention the work of Schöpf and Braun [1] who acetylated the alkaloid of isotripiperidine and our own communication [2] in which the reaction of ketene with cytisine was investigated. From this aspect we thought it of considerable interest to carry out a number of investigations on the alkaloids of anabasis and thus to extend information on the reactivity of ketene with this class of organic compounds. Numerous works on anabasine, in which it was shown that this alkaloid is a fairly powerful base, served as the starting point. The second alkaloid (by content) of Anabasis Aphylla L. is lupinine, a tertiary base.

The acetyl derivative of anabasine was described by A. S. Sadykov and O. S. Otroshchenko [3]; the corresponding derivative of lupinine is unknown. The reaction of ketene with other alkaloids of Anabasis Aphylla L. has not been studied.

As a result of the investigation carried out it was established that anabasine and lupinine are readily acetylated by ketene. Their acetyl derivatives show a marked difference as regards boiling points; in addition, o-acetyllupinine is insoluble in water whereas N-acetylanabasine is readily soluble in it. These data served as the basis for the development of a new method of separating all the alkaloids of anabasine by means of their acetyl derivatives. It was found that by this method it was possible not only to separate a mixture of anabasine and lupinine but also to obtain them in a pure form directly from the total alkaloids contained in anabasis: anabasine, aphylline, anaphylline and No. 5 base. An undoubted advantage of this method of separation is the ease of saponification of o-acetyllupinine, as a result of which lupinine is obtained easily and rapidly, in contrast to all other previously known methods.

Another characteristic feature of the acetylation of the alkaloids of anabasis by ketene is that when the ketene is passed into a mixture of anabasine and water anabasine acetate is formed in the first stage of the reaction. This indicates that in the first stage of the reaction the ketene reacts with the water and not with the secondary amino group. This observation is diametrically opposed to the established opinion that ketene reacts far more rapidly with an amino group than with water. In this connection we may briefly mention the work of Hurd and Kocaur [4] in which the authors maintain the above-mentioned opinion. The experimental section of the present work is directly contrary to the conclusions of these authors. In this connection it must be mentioned that in our previous communications we also established cases when ketene in the combined presence of an amine and water reacted primarily with the water [5].

### EXPERIMENTAL*

Preparation of N-acetylanabasine. 10 g of anabasine with a b. p. of 121-122° at 5 mm and $n_D^{20}$ 1.5412 was placed in a four-necked flask equipped with a mechanical stirrer, reflux condenser, gas feed and thermometer. The temperature of the reaction mixture rose to 70° as a result of the heat evolved. Ketene was passed for 1.5 hrs. After the reaction mixture had been distilled under vacuum two fractions were obtained: 1st fraction (anabasine), b. p. 121-122° at 5 mm, 4.3 g; 2nd fraction (acetylanabasine), b. p. 198-200° at 5 mm, 5.3 g (42%), $n_D^{20}$ 1.5547, $d^{20}$ 1.1165, $MR_D$ 58.62; calc. 59.70.

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* Yu. N. Forostyan participated in this work.

Found %: $CH_3CO$ 19.48. $C_{12}H_{16}ON_2$. Calculated %: $CH_3CO$ 21.05.

Acetylanabasine hydrochloride had a m. p. of 199-200° (from acetone).

Found %: Cl 15.49. $C_{12}H_{16}ON_2 \cdot HCl$. Calculated %: Cl 14.74.

The picrate had a m. p. of 182-183° (from alcohol).

Acetylation of anabasine in the presence of water. 30 g of anabasine was acetylated with ketene in 50 ml of acetone containing 5 ml of water. After 15 min the temperature of the reaction mixture rose to 40°. Ketene was passed for 30 min and the consumption of acetone by pyrolysis was 120 ml. After distillation under vacuum the following fractions were obtained: 1st fraction, b. p. 80-132° at 5 mm, 19.7 g; 2nd fraction, b. p. 198-200° at 5 mm, 14.3 g (acetylanabasine). The 1st fraction crystallized out on standing. After the crystals had been washed with anhydrous acetone the m. p. was 88°, corresponding to anabasine acetate. It was later found that anabasine acetate can be distilled under vacuum at 105-110° (2 mm); the yield of the pure salt was 14.4 g. If the period during which the ketene was passed was increased to 40 min the main reaction product was acetylanabasine with a yield of 92%.

The acetylation of anabasine in the presence of acetic acid was completed in 30 min; the maximum temperature of the reaction mixture was 85°, the yield of acetylanabasine was 96%.

Acetylation of anabasine acetate. 5 g of anabasine acetate with an m. p. of 88° was acetylated with ketene in 80 ml of acetone. After about 10 min the crystals began to decrease and had completely disappeared after 55 min. Ketene was passed for a further 10 min. The yield of acetylanabasine was 4.1 g.

Preparation of o-acetyllupinine. Ketene was passed into a mixture of 5 g of lupinine, 30 ml of acetone and 0.2 g of glacial acetic acid. The consumption of acetone due to pyrolysis was 120 ml, the total time for which the ketene was passed was 20 min. After the mixture had been fractionated 3 times under vacuum a yield of 5.5 g (89%) of a liquid with the following characteristics was obtained: b. p. 131-132° at 5 mm, $n_D^{20}$ 1.4900, $d^{20}$ 1.0307, $MR_D$ 59.1; calc. 58.81.

Found %: $CH_3CO$ 19.03. $C_{12}H_{21}O_2N$. Calculated %: $CH_3CO$ 20.35.

The m. p. of o-acetyllupinine hydrochloride was 200-201°.

o-Acetyllupinine was a green mobile liquid with a faint odor; it was insoluble in water but readily soluble in alcohol, acetone, ether, ethyl acetate, benzene and methanol. After the o-acetyllupinine had been boiled for 20 min with aqueous alkali and the organic part extracted with ether, lupinine with a m. p. of 68-69° was readily obtained.

Acetylation of lupinine acetate. Lupinine acetate was obtained by mixing alcoholic solutions of lupinine and acetic acid. The white precipitate formed had a m. p. of 201-202°.

Found %: $CH_3COOH$ 25.74. $C_{10}H_{19}ON \cdot CH_3COOH$. Calculated %: $CH_3COOH$ 26.18.

5 g of lupinine acetate was acetylated with ketene in 80 ml of toluene. The ketene was passed until the salt had completely dissolved. o-Acetyllupinine was obtained; the yield was 4.2 g.

Acetylation of a mixture of anabasine and lupinine. 10 g of a mixture of anabasine and lupinine with $n_D^{20}$ 1.5370 (corresponding to a lupinine content of about 15%) was dissolved in 20 ml of toluene containing 0.1 ml of glacial acetic acid. The ketene was passed for 1 hr. The maximum temperature of the reaction mixture was 42°. After the latter had been distilled under vacuum the following fractions were obtained: 1st fraction (acetylanabasine) with a b. p. of 196-200° at 5 mm, $n_D^{20}$ 1.5541, yield 80% (of the total amount of mixture); 2nd fraction (o-acetyllupinine) with a b. p. of 130-132° at 5 mm, $n_D^{20}$ 1.4900, yield 13% (of the total amount of mixture). When the 1st and 2nd fractions were saponified anabasine and lupinine were obtained, respectively.

The preparation of anabasine and lupinine from the total alkaloids of anabasis. 100 ml of a benzene solution containing 50 g of a mixture of anabasine, lupinine, aphylline, anaphylline and aphyllidine was dried with melted potash; the solution was then filtered into a four-necked flask containing 0.5 ml of glacial acetic acid. Ketene was passed for 4 hrs; the consumption of acetone was 400 ml and the temperature of the reaction mixture was 35°. After the ketene had been passed the mixture was a thick, viscous, tough, dark-brown mass which was boiled thoroughly with activated carbon. After the mixture had been filtered the benzene was distilled off and the residue was transferred to a separating funnel with water and shaken vigorously. After half an hour o-acetyllupinine settled out on the bottom of the funnel whereas the other alkaloids remained in solution. The o-acetyllupinine was boiled with alkali for 30 min and the lupinine was then extracted with ether. After it had been recrystallized from acetone a yield of 5.7 g (10% of the total alkaloids) of lupinine with an m. p. of 70° was obtained.

After the o-acetyllupinine had been separated 50 ml of concentrated hydrochloric acid was added to the remaining aqueous layer and the mixture was boiled for 20 hrs on a water bath. After it had cooled the solution was made alkaline and the alkaloids were extracted with ether. By distillation of the extract a yield of 40 g (about 80% of the mixture used) of anabasine was obtained with a b. p. of 136-139° at 10 mm and $n_D^{20}$ 1.5427.

## SUMMARY

1. Ketene can be used successfully for the acetylation of alkaloids in the presence of water or acetic acid.

2. The acetylation of anabasine with ketene in the presence of water takes place via the stage of formation of the corresponding acetate.

3. A new method was proposed for separating a mixture of the alkaloids of anabasine based on their acetyl derivatives.

4. o-Acetyllupinine, which has not been described in the literature, was obtained.

## LITERATURE CITED

[1] C. Schöpf and F. Braun, Naturw. 36, 377 (1949).

[2] Yu. V. Svetkin, J. Gen. Chem. 26, 1216 (1956). *

[3] O. S. Otroshchenko and A. S. Sadykov, J. Gen. Chem. 24, 1855 (1954). *

[4] Ch. Hurd and Kocaur, J. Am. Chem. Soc. 45, 2167 (1923).

[5] Yu. V. Svetkin, Sci. Rec. Kishinev Univ. 14 (Chem.), 67 (1855); J. Gen. Chem. 26, 1216 (1956). *

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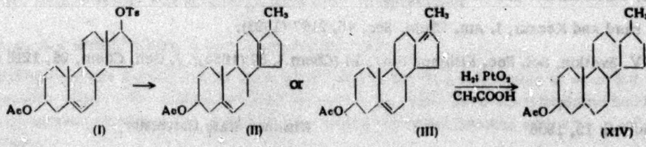
# SOME PROPERTIES OF p-TOLUENESULFONIC ACID ESTERS OF 17 β-HYDROXYSTEROIDS

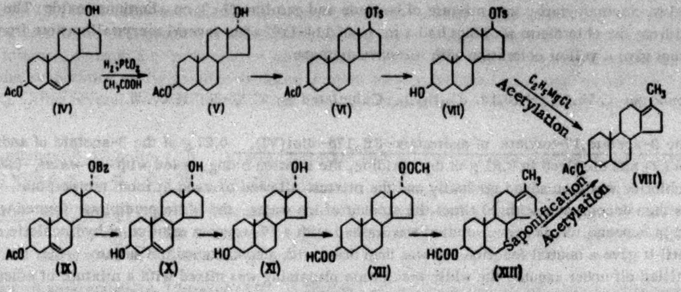
## VIII. THE POSITION OF THE DITERTIARY DOUBLE BOND OF 3-β-ACETATES OF 17-METHYL-18-NORANDROSTENOL AND ANDROSTADIENOL

O. S. Madaeva

The structure of a retro-compound of the androstane series, formed by heating androstane-3β,17α-diol (XI) with anhydrous formic acid was studied by Miescher and Kägi [1] who proved that it contains a ditertiary double bond between $C_{13}$ and $C_{17}$. Earlier [2] it was shown that the splitting off of p-toluenesulfonic acid fromthe 17-tosyl ester of the 3-acetate of $\Delta^5$-androstene-3β,17β-diol (I) is accompanied by a retro-pinacolinic rearrangement with the formation principally of a compound with a m. p. of 95-96° which also contains a ditertiary double bond. Until now, however, the position of this double bond has not been proven; it may lie between $C_{13}$ and $C_{14}$ (II) or between $C_{13}$ and $C_{17}$ (III). To prove the position it was sufficient to obtain the corresponding retro-compound of the 17β-tosyl ester of the androstane series in order to compare it with the 3-acetate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol, which is easily obtained by saponification of the formate (XIII) followed by acetylation.



Of the various methods of synthesizing retro-compounds from 17-tosyl esters of the androstene series the most interesting is the synthesis with ethylmagnesium bromide leading to an individual retro-compound with a ditertiary double bond [3]. To obtain the individual retro-compound of the androstane series, we therefore decided to react ethylmagnesium chloride with the 17-tosyl ester of androstane-3β,17β-diol (VII). The initial substance used for the synthesis of (VII) was the 3-acetate of $\Delta^5$-androstene-3β,17β-diol (IV) which after hydrogenation in glacial acetic acid with platinic oxide gave the 3-acetate of androstane-3β,17β-diol (V). Since it is extremely difficult to purify (IV) from the 17α-isomer there is a possibility that the latter was contained as an admixture in (V) also. When the 3-acetate,17-tosylate of androstane-3β,17β-diol (VI) is prepared this possibility is excluded since its isomeric 17α-tosylate is far more readily soluble in ether and passes into the filtrate when the reaction product is washed with a mixture of ether and petroleum ether. The preparation of the tosyl derivative was carried out in pyridine by the gradual addition of p-toluenesulfonylchloride. The 3-acetate,17-tosylate of androstane-3β,17β-diol (VI) was crystallized from acetone. The 17-tosyl ester of androstane-3β,17β-diol (VII) was obtained by the saponification of (VI) with a methanolic solution of caustic potash. The reaction of (VII) with ethylmagnesium chloride and the subsequent treatment were carried out under the conditions described for the 3-acetate,17-tosylate of $\Delta^5$-androstene-3β,17β-diol [3]. After acetylation the tarry residue obtained was dissolved in gasoline and purified by passing it through a column containing aluminum oxide. By recrystallizing from methanol a substance with a m. p. of 88-89.5° was obtained which showed no variation in the melting point after a second crystallization. From the ultimate analysis and on the basis of a positive Kägi and Miescher reaction [4] it corresponded to the acetate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (VIII).



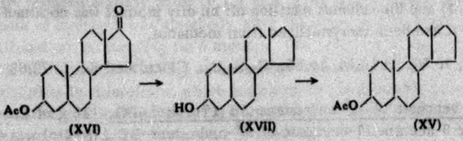
To synthesize the formate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (XIII) we used the 3-acetate, 17-benzoate of $\Delta^5$-androstene-3β,17α-diol (IX) [5], isolated from the filtrates after the separation of its 17β-isomer which is an intermediate product in the synthesis of testosterone [6].

After the saponification of (IX) with a 1N methanolic solution of caustic soda $\Delta^5$-androstene-3β,17α-diol (X) was obtained; after hydrogenation in glacial acetic acid with platinic oxide this was converted to androstane-3β-17α-diol (XI). From this was obtained the diformate of androstane-3β,17α-diol (XII) which when heated with formic acid at 90-95° gave a compound which from its ultimate analysis and melting point corresponded to the formate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (XIII) described by Miescher and Kägi. By saponification and acetylation of the latter compound a substance was obtained which in a mixed melt with a sample of (VIII), obtained from the 17β-tosyl ester of androstane-3β-ol gave no depression of the melting point.

The identity of these compounds showed that in the retro-compound, obtained by splitting off p-toluenesulfonic acid from (VII), the double bond lies between $C_{13}$ and $C_{17}$, as in the case of the retro-compound formed from the 17α-formate (described by Miescher and Kägi) and is, therefore, a ditertiary type.

The fact that individual retro-compounds with a ditertiary double bond both of the androstane and the androstene series are obtained from 17β-tosyl esters and are obtained under like conditions (reaction with ethylmagnesium chloride) justifies the assumption that when p-toluenesulfonic acid is split off from 17β-tosylates the ditertiary double bond is formed only between $C_{13}$ and $C_{17}$.

The change in the carbon skeleton which takes place when p-toluenesulfonic acid is split off from the 17β-isomer of the tosyl ester (I) was proven by comparing the acetate of retro-androstane-3β-ol (XIV) (m. p. 96-98°) – the product of exhaustive hydrogenation (III) – with the acetate of androstane-3β-ol (XV) (m. p. 85.5-87°), obtained by the reduction of androstane-3β-17-one (XVI) under the conditions of the Kischner-Wolff method (modified) [8] followed by the acetylation of androstane-3β-ol (XVII). A mixed melt of (XIV) and (XV) showed a marked depression of the melting point.



## EXPERIMENTAL

**The 3-acetate of androstane-3β,17β-diol (V).** 1.7 g of the 3-acetate of $\Delta^5$-androstene-3β,17β-diol (IV) with m. p. of 142-143.5° was hydrogenated in 52 ml of glacial acetic acid in presence of preliminarily reduced platinic oxide (0.1 g in 25 ml of glacial acetic acid). After the usual treatment the precipitate obtained was subjected to chromatography in a mixture of benzene and gasoline (1:3) on aluminum oxide. The precipitate obtained from the chloroform washings had a m. p. of 114-116° after several recrystallizations from methanol and did not give a yellow coloration with tetranitromethane.

Found %: C 75.15; H 10.13. $C_{21}H_{34}O_3$. Calculated %: C 75.38; H 10.25.

**The 3-acetate,17-tosylate of androstane-3β,17β-diol(VI).** 0.27 g of the 3-acetate of androstane-3β, 17β-diol (V) was dissolved in 0.81 g of dry pyridine, the solution being cooled with ice water; 0.36 g of p-toluenesulfonylchloride was then added gradually and the mixture allowed to stand at room temperature. The reaction mass was then decomposed with 10 times the amount of ice water; the white precipitate formed was filtered off, dissolved in benzene, the benzene solution was washed with a 5% aqueous solution of hydrochloric acid and with water until it gave a neutral reaction and was then dried with anhydrous sodium sulfate. After the benzene had been distilled off under vacuum the white precipitate remaining was mixed with a mixture of ether and petroleum ether (2:1); 0.28 g of a substance with a m. p. of 170-171° was obtained; a further 0.02 g of a substance with a m. p. of 168-170° was isolated from the filtrate. Both precipitates were recrystallized from acetone and compound (VI) with a m. p. of 173-174.5° was isolated.

Found %: C 68.75; H 8.08; S 6.74. $C_{28}H_{40}O_5S$. Calculated %: C 68.81; H 8.25; S 6.55.

**The 17-tosylate of androstane-3β,17β-diol (VII).** 0.2 g of (VI) was boiled with a methanolic solution of caustic potash (0.24 g of KOH in 16.6 ml of methanol) for 1.5 hrs. After the methanol had been reduced to a small volume by distillation the precipitate was decomposed with water, the white precipitate formed was extracted with ether and the ether extract washed with water until it gave a neutral reaction; after the ether had been distilled off, the precipitate (0.12 g) was recrystallized twice from methanol and then from ether; clusters of needles with a m. p. of 131-132° were obtained.

Found %: C 69.67; H 8.68; S 7.09, 6.96. $C_{26}H_{38}O_4S$. Calculated %: C 69.90; H 8.58; S 7.17.

**The acetate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (VIII).** 20 ml of an ethereal solution of ethylmagnesium chloride (4.18%) was added to a boiling ethereal solution of 0.7 g of (VII); a white flocculent precipitate was formed immediately. After 15 min about 35 ml of ether was distilled off from the reaction mass and 25 ml of anhydrous benzene was then added; after 7-10 ml of the mixture of solvents had been driven off boiling was continued for a further 2 hrs 15 min. Toward the end of this period a thick, jelly-like mass was formed in the flask. After it had been decomposed with water and acidified with 3% sulfuric acid the ethereal layer was washed with water until it gave a neutral reaction and chlorine could no longer be detected in the wash water; it was then dried over calcined sodium sulfate. After the ether had been distilled off 0.56 g of a slightly yellowish oil was obtained which gave a positive Kägi and Miescher reaction and did not contain halogen. To isolate pure (VIII) the precipitate obtained was acetylated: 0.56 g of the oil was dissolved in 2.24 ml of anhydrous pyridine, 0.56 g of acetic anhydride was added and the mixture left for 24 hrs at room temperature. After the usual treatment 0.56 g of an almost colorless oil was obtained; this was dissolved in 10 ml of gasoline (b. p. 60-80°) and passed through a column containing aluminum oxide. After the column had been washed with a gasoline-benzene mixture (1:1) and the solvents distilled off an oily product was obtained which gave platelets with a m. p. of 88-89.5° after it had been recrystallized from methanol.

Found %: C 79.63, 79.76; H 10.34, 10.55. $C_{22}H_{31}O_2$. Calculated %: C 79.68; H 10.20.

**The 3-acetate, 17-benzoate of $\Delta^5$-androstene-3β,17α-diol (IX).** 15 g of the dark tarry mass obtained after the separation of the 3-acetate,17-benzoate of $\Delta^5$-androstene-3β,17β-diol was dissolved in 150 ml of ether; the ethereal solution was washed with a 5% solution of alkali to free it from admixtures of pyridine and it was then washed with water. After the ethereal solution had been dried with sodium sulfate the ether was distilled off. 9 g of a tarry residue was obtained and dissolved in 150 ml of a mixture of gasoline (b. p. 60-80°) and benzene (4 : 1); the solution was passed through 160 g of aluminum oxide in a column which was washed with the same mixture of solvents. The washing fractions were collected in 50 ml lots until a solution of the investigated sample in glacial acetic acid did not give a blue color when boiled with a few drops of chemically pure sulfuric acid, a test which is characteristic for 17α-esters. All the washings which gave a positive reaction for the 17α-benzoate (IX) were collected together and after the solvent had been distilled off isopropyl alcohol was added; 5 g of a crystalline precipitate was obtained which was passed a second time, under the same conditions as in the first instance, through a column containing aluminum oxide. The middle washing fractions were collected and after the evaporation of the gasoline-benzene mixture they crystallized from ether as needles, characteristic for (IX). After several recrystallizations from isopropyl ether 1.5 g of (IX) with a m. p. of 130-131° was obtained.

$\Delta^{5}$-Androstene-3β,17α-diol (XI). (IX) was saponified with a 1N methanolic solution of caustic soda [5]. Compound (X) with a m. p. of 195-198.5° was obtained.

Androstane-3β,17α-diol (XI). $\Delta^{5}$-Androstene-3β,17α-diol (X) was hydrogenated in glacial acetic acid with platinic oxide. After appropriate treatment the precipitate formed (XI) did not give a yellow color with tetranitromethane and melted at 212.5-213.5° [5].

Diformate of androstane-3β,17α-diol (XII). 0.56 g of (XI) was carefully heated with 3 ml of freshly-distilled 99% formic acid at 30-40°. After 11 min all the precipitate had gone into solution; heating was continued at 25-30° for 2 hrs. Towards the end of this period the entire mass crystallized out and a slightly bluish tint appeared. The precipitate was separated from the liquid, washed with water (until a neutral reaction was obtained) and with 2 ml of a mixture of petroleum ether and acetone. 0.65 g of (XII) was obtained. When it had been dried at 45° under the vacuum produced by a water-jet pump the diformate melted at 152-154°.

Formate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (XIII). 0.3 g of (XII) was carefully heated with 1.5 ml of 99% formic acid. The precipitate rapidly passed into solution and heating was continued for 50 min, the solution gradually turning blue and then becoming dark-violet; a layer of colorless oil separated out at the top. After extraction with petroleum ether the extracts obtained were washed twice with formic acid, ice water, sodium bicarbonate solution and then with water again until a neutral reaction was obtained. The extracts were dried over calcined sodium sulfate; the petroleum ether was driven off until only a small quantity remained and 0.11 g of a crystalline substance which did not give a Kägi and Miescher reaction was obtained. When anhydrous alcohol was added to the filtrate, compound (XIII) with a m. p. of 109-110° was precipitated.

Found %: C 79.62; H 10.08. $C_{20}H_{30}O_2$. Calculated %: C 79.41; H 10.00.

The acetate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (VIII). 0.1 g of (XII) was saponified with an aqueous-methanolic solution of potash (0.1 g of $K_2CO_3$ + 0.6 ml of $H_2O$ + 7 ml of $CH_3OH$), the mixture being boiled for 1 hr 15 min. After the usual treatment the colorless oil obtained was acetylated in pyridine with acetic anhydride at room temperature for 24 hrs; it was then poured into water, extracted with ether and the ethereal layer was washed free from acid with water and dried over sodium sulfate. After the ether had been distilled off the oily residue obtained (0.09 g) was dissolved in gasoline and transferred to aluminum oxide. A white crystalline precipitate was deposited from the first washings and after recrystallization from methanol this melted at 87-88.5° and gave a definite Kägi and Miescher reaction; a mixed melt with a sample of the acetylated reaction product of (VII) with ethylmagnesium chloride showed no depression of the melting point.

The acetate of 17-methyl-18-norandrostane-3β-ol (XIV). 0.1 g of (III) was exhaustively hydrogenated in the presence of preliminarily reduced platinic oxide (0.1 g in 4 ml of glacial acetic acid) in 5 ml of glacial acetic acid. The theoretical amount of hydrogen was absorbed; after the usual treatment 0.1 g of a light-yellow oil was obtained, which crystallized out on standing for 5 months. The precipitate was recrystallized from ethyl alcohol, the m. p. being 92-98°; it did not give a Kägi and Miescher reaction, a color with tetranitromethane or a reaction with antimony trichloride in chloroform, which indicates that both double bonds had been completely hydrogenated. After a second recrystallization from ethyl alcohol elongated platelets with a m. p. of 96-98° were obtained. A mixed melt of (XIV) and (XV) melted at about 70°.

Found %: C 79.03; H 10.71. $C_{21}H_{34}O_2$. Calculated %: C 79.17; H 10.76.

Androstane-3β-ol (XVII). 0.2 ml of hydrazine hydrate and sodium diethylene glycolate (prepared from 0.05 g of sodium in 3 ml of diethylene glycol) was added to a solution of 0.2 g of (XVI) in 7 ml of diethylene glycol and heated for 2 hrs at a bath temperature of 200° and then for a further 3 hrs at 210-213°. After it had cooled, the solution which had turned slightly yellow was poured into 25 ml of water, acidified with 4N hydrochloric acid and extracted with ether. The ether was evaporated and the precipitate obtained was crystallized from acetone; it melted at 148-148.5° [7].

The acetate of androstane-3β-ol (XV). 0.07 g of (XVII) was dissolved in 0.3 g of pyridine, 0.1 g of acetic anhydride was added and the mixture was left at room temperature for 24 hrs. After the usual treatment a tarry crystalline precipitate (0.07 g) was obtained, which after it had been crystallized from aqueous acetone formed clusters of long needles with a m. p. of 85.5-87°.

## SUMMARY

1. An "individual retro-compound" of the androstane series – acetate of 17-methyl-18-nor-$\Delta^{13,17}$-androstene-3β-ol (VIII) – was obtained.

2. The location of the ditertiary double bond between $C_{13}$ and $C_{17}$ in the main product obtained by the splitting off of p-toluenesulfonic acid from 17β-tosyl esters both of the androstane and androstene series was proven.

3. It was shown that the "individual retro-compound" with a m. p. of 96-98° (XIV) has the unchanged carbon skeleton of the steroids.

## LITERATURE CITED

[1] K. Miescher and H. Kägi, Helv. Chim. Acta 32, 761 (1949).

[2] O. S. Madaeva and F. A. Luryi, Proc. Acad. Sci. USSR 84, 713 (1952).

[3] O. S. Madaeva, J. Gen. Chem. 25, 1427 (1955).*

[4] H. Kägi and K. Miescher, Helv. Chim. Acta 22, 683 (1939).

[5] L. Ruzicka and H. Kägi, Helv. Chim. Acta 19, 842 (1936).

[6] L. Ruzicka, A. Wettstein, and H. Kägi, Helv. Chim. Acta, 18, 1478 (1935).

[7] R. D. H. Heard and A. F. McKay, J. Biol. Chem. 165, 677 (1946).

[8] Huang-Minlon, J. Am. Chem. Soc. 68, 2487 (1946).

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Chemical-Pharmaceutical Institute

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# REACTIONS OF DIKETENE

## V. THE REACTION OF DIKETENE WITH DIHYROXYNAPHTHALENES

V. V. Perekalin and G. D. Padva

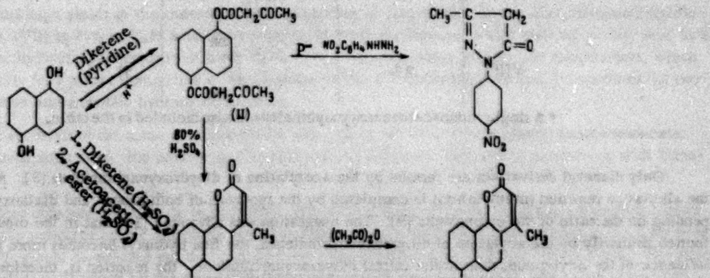
The reaction of diketene with aromatic hydroxy compounds has attracted the attention of investigators because of the possibility of a simple method of synthesizing difficultly obtainable aceto-acetic esters of phenols which are not formed when phenols react with aceto-acetic esters and the possibility of the heterocyclicization of o-acetoacetylphenols into derivatives of the coumarin series.

The following facts are known with regard to the reaction of diketene with aromatic hydroxy compounds, principally phenols: 1) in the presence of basic [1-3] and acid [1, 2,4] catalysts the initial substances form aceto-acetic esters of phenols, with high yields, 2) in excess sulfuric acid [3] and with aluminum chloride [5] these esters are cyclicized into coumarin derivatives, 3) by the reaction, discovered by one of us together with K. B. Rall, coumarins are formed by the direct reaction of diketene with a number of aromatic hydroxy compounds in ether in the presence of sulfuric acid [5-7].

In order to extend the field of aromatic compounds which react with diketene and to discover new methods of synthesizing coumarin derivatives we investigated the reaction of diketene with a series of dihydroxynaphthalenes. The diacetoacetoxynaphthalenes (I)-(VII) (Table 1) were synthesized from 1,4-, 1,5-, 1,8-, 1,2-, 1,7-, 2,6- and 2,7-dihydroxynaphthalenes and 2 moles of diketene in the presence of pyridine and benzene. Acid catalysts (sulfuric acid, phosphorus oxychloride) in accordance with the previously-considered mechanism [6] also favor the reaction (but to a lesser degree); dihydroxynaphthalenes are not acetoacetylated by diketene without the use of catalysts.

In order to establish the structure the diacetoacetoxynaphthalenes obtained were hydrolyzed and introduced in the reaction with p-nitrophenylhydrazine. Heating with dilute hydrochloric acid led to the formation of the initial dihydroxynaphthalenes and acetone, the 1,5-acetoacetoxynaphthalene (II) being found to be particularly unstable to hydrolysis and decomposed by heating with 96% ethanol. All the acetoacetoxy derivatives reacted with p-nitrophenylhydrazine on account of their acetoacetyl groups and formed methyl-p-nitrophenylpyrazolone.

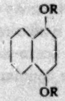
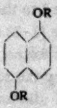
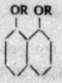
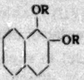
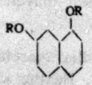
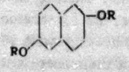
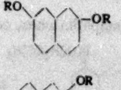
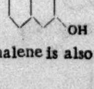
The structure of the diacetoacetoxynaphthalenes, confirmed by analytical data, was, therefore, not open to question.



The reduction in the yield of 1,2-diacetoacetoxynaphthalene (IV) compared to the yields of other diacetoacetoxy derivatives and the synthesis of only the monoacetoacetoxy derivative (VIII) from 2,3-dihydroxynaphthalene was possibly caused by the blocking of the hydrogen atom by one of the hydroxyl groups as a result of the formation by the latter of an intramolecular hydrogen bond. The fact that attempts to form monoacyl derivatives of dihydroxynaphthalenes (with the exception of 2,3-dihydroxynaphthalene) were unsuccessful is worthy of note. The reaction of dihydroxynaphthalenes with 1 mole of diketene was completed by the formation of diacetoacetoxynaphthalenes with yields which were half those obtained when they reacted with 2 moles of diketene and by the liberation of the dihydroxynaphthalene which had not taken part in the reaction.

TABLE 1

Diacetoacetoxynaphthalenes

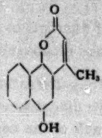
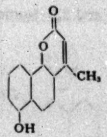
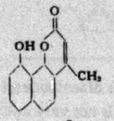
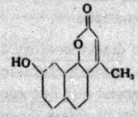
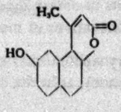
| No. of compound | Position of the acetoacetoxy groups | Structural formula | Yield (as %) |
|---|---|---|---|
| I | 1,4- |  | 73 |
| II | 1,5- |  | 91 |
| III | 1,8- |  | 59 |
| IV | 1,2- |  | 32 |
| V | 1,7- |  | 59 |
| VI | 2,6- |  | 45 |
| VII | 2,7- |  | 78 |
| VIII * | 2,3- |  | 57 |

* A single monoacetoacetoxynaphthalene is also included in the table.

Only diacetyl derivatives are formed by the acetylation of dihydroxynaphthalenes [8]. At the same time the alkylation reaction (methylation) is completed by the synthesis of both mono- and dialkoxynaphthalenes, depending on the ratio of the components [9]. The suggestion was advanced [10] that in the monoacyl derivative, formed primarily by the acylation of dihydroxynaphthalenes, the free hydroxyl becomes more reactive, under the influence of the acyl group, than in the initial dihydroxynaphthalene; the reaction is, therefore, directed toward the formation of only diacylated dihydroxynaphthalenes; the alkyl group in monoalkylated dihydroxynaphthalenes does not, however, appreciably alter the activity of the unsubstituted hydroxy group.

**TABLE 2**

Coumarin Derivatives of Dihydroxynaphthalenes

| No. of compound | Name | Structural formula | Yield (as %) | | |
|---|---|---|---|---|---|
| | | | From dihydroxynaphthalenes by the action of | | From diacetoacetoxynaphthalenes (calc. on the basis of dihydroxynaphthalenes). |
| | | | Diketene | Acetoacetic ester | |
| IX | 4-Methyl-6-hydroxy-7,8-benzocoumarin |  | 75 | 95 | 68.6 |
| X | 4-Methyl-7,8-(4'-hydroxybenzo)-coumarin |  | 86 | 79 | 90.8 |
| XI | 4-Methyl-7,8(1'-hydroxybenzo)-coumarin |  | 89 | 88 | 55 |
| XII | 4-Methyl-7,8-(2'-hydroxybenzo)-coumarin |  | 78 | 88 | 56 |
| XIII | 4-Methyl-5,6-(2'-hydroxybenzo)-coumarin |  | 59 | 67 | 72.7 |

The second task of the investigation — the synthesis of coumarins from diketenes and dihydroxynaphthalenes (Table 2) — was resolved by two methods: 1) the initial components in a five-molar excess of 96% sulfuric acid immediately formed high yields of the monocoumarin derivatives of (IX)-(XIII); 2) the diacetoacetoxynaphthalenes (I)-(III), (V), (VII) in 80% sulfuric acid (converted to dihydroxynaphthalenes with reduced yields) were heterocyclized into methylhydroxybenzocoumarins due to the one acetoacetoxy group. The first method, which was used successfully for hydroxy compounds of the benzene series, is a convenient method for synthesizing coumarins from diketene and aromatic hydroxy compounds.

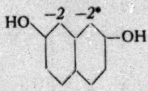
Finally, the synthesis of the same monocoumarins was carried out by a third method: from acetoacetic ester and dihydroxynaphthalenes; the coumarins (IX) [11] and (X) [12] were obtained in accordance with literature data.

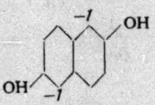
The substances obtained were stable to hydrolysis, dissolved in dilute alkalis and formed acetylcoumarins (XIV)-(XVIII) by the action of acetic anhydride and, therefore, contained a free hydroxyl group, i. e., they were monocoumarins. It should be pointed out that hydroxycoumarins are not acetoacetylated by diketene. The structure of the coumarins, synthesized by the three different methods, was not, for the most part, open to question [(IX), (X), (XI), (XVIII)] since in the initial dihydroxynaphthalenes or their diacetoacetyl derivatives there was only one possibility of monoheterocyclicization on account of the hydroxyl and then only of β-[(I), (II), (III)] or α-[(VII)]-carbon atoms of the ring. It is only in 1,7-dihydroxynaphthalene that the heterocycle can be formed in two ways: with the participation of the α- or β-positions (V).

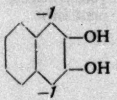
In the present work and previously conducted investigations it was shown, however, that the formation of methylbenzocoumarin from diketene [6] or acetoacetic ester [13, 14] and 1-naphthol, and also 1-acetoacetoxynaphthalene (α-cyclicization) proceeded smoothly, giving yields which were almost quantitative, whereas it was only possible to synthesize coumarin from 2-naphthol (β-cyclicization) with great difficulty (when diketene in sulfuric acid was used the yield was only 3%). It has not yet proved possible, however, to heterocyclicize 2-acetoacetoxynaphthol. The coumarin (XII) was, therefore, formed according to the 1-naphthol type.

These same reasons were the cause of the failure of attempts to synthesize coumarins from 2,6- and 2,3-dihydroxynaphthalenes and by the same token, their di- and monoacetoacetyl derivatives.

Finally, it is necessary to explain the example of β-cyclicization in the formation of hydroxybenzocoumarin from diketene and 2,7-dihydroxynaphthalene and its diacetoacetyl derivative. The cause evidently consists in the fact that in 2,7-dihydroxynaphthalene, as a result of the coordinated orientation of the hydroxyl groups, the activity of the α-position is greater than in the 2,6- and 2,3-isomers where the hydroxyl groups activate the naphthalene ring in an uncoordinated manner.







The structure of 1,2-dihydroxynaphthalene and its diacetoacetyl derivatives excluded the possibility of cyclicization (the 3-position in naphthalene derivatives is not very active but a seven-membered ring based on the 8 position is not justified with respect to energy relationships).

The mechanism of the heterocyclicization of the diacetoacetoxy derivatives is as follows: 1) a monocoumarin ring is formed by the splitting off of water; 2) as a result of the reduction in the activity of the unsubstituted positions of the naphthalene ring closure of the second ring becomes difficult and the second acetoacetyl group is saponified. This explains the failure of attempts to obtain dicoumarins from dihydroxy naphthalenes and diketene and also of attempts to isolate acetoacetoxy derivatives of monocoumarins.

In the direct synthesis of coumarins from dihydroxynaphthalenes and diketene or acetoacetic ester the reaction proceeds (with greater reliability in the latter instance), as in the case of carbylation of phenols, in the ortho position to hydroxyl followed by closure of the ring [6].

## EXPERIMENTAL

1,4-, 1,5-, 1,8-, 1,2-, 1,7-, 2,6-, 2,7-, and 2,3-dihydroxynaphthalenes were obtained by previously-described methods [15-22].

Examples of the syntheses, typical for each group of substances, are given below. Deviations from the general methods and specific features of the individual substances are mentioned separately. The analytical data and the melting points are given in Tables 3-5.

### I. The Preparation of Diacetoacetoxynaphthalenes

**1,4-Diacetoacetoxynaphthalene (I).** A solution of 2.0 g (0.023 mole) of 96-97% diketene in 5 ml of benzene was added gradually to a suspension of 1.6 g (0.01 mole) of 1,4-dihydroxynaphthalene in 20 ml of benzene containing 2 drops of pyridine and the mixture was heated to boiling. After it had been boiled for 2 hrs and the odor of diketene had disappeared the hot solution was filtered and concentrated to a volume of 5 ml; after it had cooled a precipitate was formed and this was separated and washed several times with small amounts of ether.

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* The indices signify the comparative activity.

## TABLE 3

**Acetoacetoxynaphthalenes**

| No. of compound | Melting point | Analytical data (as %) | | |
|---|---|---|---|---|
| | | C | H | M |
| I | 123—124° | 66.17. 65.97 | 5.18. 5.19 | 314. 310 |
| II | 152—153 | 66.01. 65.48 | 5.19. 5.04 | 303. 340 |
| III | 126—127 | 65.89. 66.17 | 5.15. 4.19 | 320. 300 |
| IV | 93—94 | 66.01. 65.87 | 5.18. 5.14 | 306. 312 |
| V | 83—84 | 66.10. 65.91 | 5.13. 5.07 | 323. 338 |
| VI | 125—126 | 65.99. 66.02 | 5.18. 5.18 | 298. 350 |
| VII | 122—123 | 65.72. 65.94 | 5.16. 5.14 | 301. 310 |
| VIII | 121.5—122 | 68.40. 68.81 | 5.34. 5.25 | 231. 226 |
| | | Calculated | | |
| For I—VII | | 65.85 | 4.88 | 328 |
| VIII | | 68.85 | 4.92 | 244 |

## TABLE 4

**Coumarins**

| No. of compound | Melting point | Analytical data (as %) | |
|---|---|---|---|
| | | C | H |
| IX | 281—282° Ethanol | 74.04. 74.69 | 4.70. 4.69 |
| X | 296—299 Aqueous pyridine | — | — |
| XI | 218—219 Carbon tetrachloride | 74.45. 74.07 | 4.58. 4.61 |
| XII | 275—276 Ethanol | 74.23. 74.38 | 4.65. 4.61 |
| XIII | 268—270 Ethanol | 74.38. 74.34 | 4.73 4.67 |
| | | Calculated | |
| | | 74.33 | 4.42 |

## TABLE 5

**Acetylcoumarins**

| No. of compound | Melting point | Analytical data (as %) | | |
|---|---|---|---|---|
| | | C | H | M |
| XIV | 187.5—188° Ethanol | 71.84. 71.84 | 4.76. 4.84 | 269. 265 |
| XV | 204 Ethanol | 71.43. 71.46 | 4.76. 4.90 | 253. 250 |
| XVI | 202 Ethanol | 71.71. 71.76 | 4.71. 4.93 | 280. 274 |
| XVII | 172 Aqueous acetone | 71.78. 71.74 | 4.57. 4.34 | 270. 259 |
| XVIII | 204 Acetone | 71.69. 71.72 | 4.78. 4.85 | 280. 278 |
| | | Calculated | | |
| | | 71.64 | 4.48 | 268 |

The compound (I) was in the form of slightly colored crystals, readily soluble in acetone, difficultly soluble in ethanol, chloroform and benzene and insoluble in ether; attempts to recrystallize it resulted in partial hydrolysis.

**1,2-Diacetoacetoxynaphthalene (IV)** was obtained in the form of an oil which crystallized after treatment with ether.

**2-Hydroxy-3-acetoacetoxynaphthalene (VIII)** was synthesized with a somewhat better yield by reacting with 1 instead of 2 moles of diketene.

### The Hydrolysis of 1,4-Diacetoacetoxynaphthalene

A suspension of 0.15 g of (I) in 10 ml of 5% hydrochloric acid was heated for 1 hr on a boiling water bath. After the solution, which was filtered hot, had cooled the initial 1,4-dihydroxynaphthalene was precipitated. The yield was 0.07 g (96%). The m. p. was 174-175°. A mixed melt with a sample of 1,4-dihydroxynaphthalene (m. p. 176-177°) had a m. p. of 175-176°. Acetone was detected qualitatively in the filtrate by the reaction with o-nitrobenzaldehyde (formation of indigo).

### The Reaction of 1,4-Diacetoacetoxynaphthalene with p-Nitrophenylhydrazine

A solution of 0.3 g (0.002 mole) of p-nitrophenylhydrazine in 15 ml of ethanol and 2 drops of glacial acetic acid was added to a solution of 0.328 g (0.001 mole) of (II) in 20 ml of ethanol, the latter solution being heated to boiling. A precipitate was formed after 24 hrs; the m. p. was 211-212° (from ethanol). A mixed melt with methyl-p-nitrophenylpyrazolone (m. p. 218°) had a m. p. of 216-217°.

The reaction of (I) with p-nitrophenylhydrazine proceeded for 1 hr in glacial acetic acid. (V) reacted with p-nitrophenylhydrazine in dioxane for two days.

The yields of p-nitrophenylpyrazolones from (I)-(VIII) were 80, 70, 70, 48, 62, 32, 62, and 62%, respectively.

## II. 4-Methyl-6-hydroxy-7,8-benzocoumarin (IX).

**a) From diketene and 1,4-dihydroxynaphthalene.** 2.8 g of 96% sulfuric acid (excess of 5 moles) was added gradually to a solution of 1.6 g (0.01 mole) of 1,4-dihydroxynaphthalene in 2.0 g of 96% diketene (0.023 mole) in 3 ml of ether* cooled to −10°. After being kept for 5 hrs at room temperature the reaction mixture was poured onto finely-crushed ice. The brown-red precipitate of (IX) which was formed (brown-red platelets after recrystallization) was difficultly soluble with heating in alcohol and acetone; it was unchanged as a result of heating it in dilute alkaline solutions and hydrochloric acid suspensions.

**b) From 1,4-diacetoacetoxynaphthalene (I).** 2.1 g (0.0064 mole) of (I) was dissolved at 0° in 10 ml of 80% sulfuric acid; a green solution was formed which gradually turned brown-red. After the solution had been kept for 2 hrs at room temperature an orange-red product began to be deposited from it. After 24 hrs the reaction mixture was poured onto ice, the precipitate was separated and washed with water. The m. p. was 281-282° (from alcohol). A mixed melt with the coumarin (IX) did not show a depression of the melting point.

**c) From 1,4-dihydroxynaphthalene and acetoacetic ester.** Sulfuric acid (96%; excess of 5 moles) was added gradually at 0°. The mixture was kept at room temperature for 5 hrs. A brown-red precipitate was formed when the mixture was poured onto ice. A mixed melt of the purified product and (IX) showed no depression of the melting point.

## III. 4-Methyl-6-acetoxy-7,8-benzocoumarin (XIV).

0.2 g of (IX) was boiled for 1 hr with 3 ml of acetic anhydride. After it had been evaporated a brown crystalline precipitate remained, which was insoluble in dilute alkalis in the cold. The m. p. was 187.5-188° (from alcohol).

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* In the presence of ether the yield of coumarin is reduced by about 5-10%.

## SUMMARY

1. In the presence of basic and acid catalysts diketene reacts with dihydroxynaphthalenes and forms acetoacetoxynaphthalenes.

2. A new modification of the synthesis of coumarins from diketene and aromatic hydroxy compounds in excess concentrated sulfuric acid was proposed.

3. Acetoacetoxynaphthalenes are converted with high yields into monocoumarin derivatives in 80% sulfuric acid.

## LITERATURE CITED

[1] K. B. Rall and V. V. Perekalin, J. Appl. Chem. 25, 1330 (1952).*

[2] K. B. Rall and V. V. Perekalin, J. Gen. Chem. 25, 276 (1955). *

[3] R. Lacey, J. Chem. Soc. 1954, 816.

[4] U. S. Patent 2180953; C. A. 1940, 1685.

[5] K. B. Rall and V. V. Perekalin, Proc. Acad. Sci. USSR 100, 715 (1955).

[6] K. B. Rall and V. V. Perekalin , J. Gen. Chem. 25, 815 (1955).*

[7] K. B. Rall and V. V. Perekalin, Author's Certificate 100409 (1054).

[8] A. Claus, J. pr. Chem. 39, 316 (1889); A. Clausius, Ber. 23, 520 (1890); P. Friedländer and H. Rudt, Ber. 29, 1069 (1896).

[9] P. Friedländer and L. Silberstern, Monatsh. 23, 513 (1902); H. Kaufmann and K. Keisswenger, Ber. 36, 569 (1903); H. Bunzly and H. Decker, Ber. 38, 3272 (1905).

[10] L. Palfray and A. Leman, Compt. rend. 200, 1328 (1935); A. Leman, Compt. rend. 202, 579 (1936); Ann. Chim. (11) 9, 357 (1938).

[11] R. Desai and S. Sethna, J. Indian Chem. Soc. 28, 213 (1951).

[12] R. Robinson and F. Weygand, J. Chem. Soc. 1941, 386.

[13] Bartsch, Ber. 36, 1966 (1933); Chacravarti, J. Indian Chem. Soc. 8, 407 (1933).

[14] A. Bocovescu, Ber. 43, 1280 (1910); Chacravarti, J. Indian Chem. Soc. 9, 389 (1932).

[15] F. Russig, J. pr. Chem. (2), 62, 32 (1900).

[16] A. Bernthsen and A. Semper, Ber. 938a (1887).

[17] H. Erdmann, Lieb. Ann. 247, 355 (1888).

[18] L. Paul, Z. Ang. Chem. 10, 24 (1891); F. Russig, J. pr. Chem. (2), 62, 32 (1900).

[19] A. Leman, Ann. Chim. 9, 356 (1938).

[20] A. Emmert, Leib. Ann. 241, 371 (1887).

[21] Schultz, Ber. 20, 3161 (1887).

[22] P. Friedländer and S. Zanzewski, Ber. 27, 761 (1894).

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* Original Russian pagination. See C.B. Translation.

# N-THIAZOLYL- AND N-PYRIDYL- DERIVATIVES OF CARBAMIDO-N'-PHOSPHORIC ACID

A. V. Kirsanov and E. S. Levchenko

In a previous work [1] it was shown that when the acyl chloride of isocyanatophosphoric acid reacts with aromatic amines, equimolecular proportions of the reacting substances being used, the addition of the amines takes place at the isocyanate group. The reaction products are acyl chlorides of N-arylcarbamido-N'-phosphoric acids. The acyl chloride of isocyanatophosphoric acid also reacts in a similar way with amines of the heterocyclic series (2-aminobenzothiazole, 2-aminothiazole, α-aminopyridine), forming the acyl chlorides of substituted carbamidophosphoric acids of the type $Cl_2PONHCONHR$ (R = heterocyclic group), which are crystalline substances hydrolyzing very readily under the influence of atmospheric moisture. The properties of these compounds differ somewhat from those of the acyl chlorides of arylcarbamidophosphoric acids which are readily hydrolyzed by water with the formation of phosphoric acid and arylcarbamides.

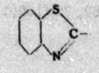
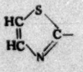
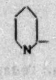
$$Cl_2PONHCONHAr + 3H_2O \rightarrow H_2NCONHAr + 2HCl + H_3PO_4$$

When hydrolyzed by water the acyl chlorides of 2-benzothiazolyl-, 2-thiazolyl- and 2-pyridylcarbamido-N'-phosphoric acid form the corresponding derivatives of phosphoric acid, which under the conditions of the reaction are not subjected to further hydrolysis.

$$Cl_2PONHCONHR + 2H_2O \rightarrow 2HCl + RNHCONHPO(OH)_2$$

TABLE 1

Compounds of the type $RNHCONHPO(OH)_2$

| No. of compound | R | Yield (as %) | Melting point (with decomp) | Found |  | Empirical molecular formula | Calc. % of N |
|---|---|---|---|---|---|---|---|
|  |  |  |  | % N | equiv |  |  |
| (I) |  | 85 | 305—310° | 15.20,<br>15.24 | 2.03,<br>2.05 | $C_8H_8O_4N_3PS$ | 15.50 |
| (II) |  | 72 | 156—158 | 18.68,<br>18.50 | 2.09,<br>1.96 | $C_4H_6O_4N_3PS$ | 18.83 |
| (III) |  | 52 | 160—162 | 18.81,<br>18.79 | 1.95,<br>1.90 | $C_6H_8O_4N_3P$ | 19.35 |

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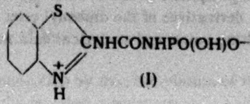
* For all the compounds the equiv. was calculated as 2.00.

The yields, melting points and analytical data of the products obtained are given in Table 1.

The N-heterocyclic derivatives of carbamido-N'-phosphoric acid are colorless, finely crystalline substances, insoluble in water and the usual organic solvents. They probably have a betaine structure (example (I)), since they readily dissolve in solutions of alkalis and are insoluble in hydrochloric acid.



(I)

When the acyl chloride of N-(2-pyridyl)-carbamido-N'-phosphoric acid is heated with water, 2-pyridylurea is formed in addition to N-(2-pyridyl)-carbamido-N'-phosphoric acid (III).

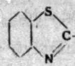
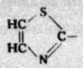
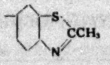
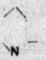
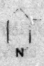
When the dimethyl ester of isocyanatophosphoric acid [2] reacts with 2-aminobenzothiazole, 2-aminothiazole, 2-methyl-6-aminobenzothiazole and α- and β-aminopyridines N-heterocyclic derivatives of the dimethyl ester of carbamido-N'-phosphoric acid are formed according to the system

$$(CH_3O)_2PONCO + R'NH_2 \rightarrow (CH_3O)_2PONHCONHR'$$

The yields, melting points and analytical data of these substances are given in Table 2.

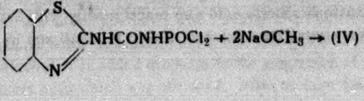
TABLE 2

Compounds of the Type $(CH_3O)_2PONHCONHR$

| No. of compound | R | Yield (as %) | Melting point | Found % N | Empirical molecular formula | Calc. % N |
|---|---|---|---|---|---|---|
| (IV) |  | 75 | 157—158° | 13.93, 13.75 | $C_{10}H_{12}O_4N_3PS$ | 13.95 |
| (V) |  | 90 | 129—130 | 16.23, 16.32 | $C_6H_{10}O_4N_3PS$ | 16.73 |
| (VI) |  | 53 | 154—156 | 13.11, 13.25 | $C_{11}H_{14}O_4N_3PS$ | 13.33 |
| (VII) |  | 88 | 154—155 | 17.05, 16.89 | $C_8H_{12}O_4N_3P$ | 17.14 |
| (VIII) |  | 56 | 160—161 | 17.45, 17.43 | $C_8H_{12}O_4N_3P$ | 17.14 |

Compounds (IV-VIII) are colorless, crystalline substances of an amphoteric character, readily soluble in both alkalis and acids. They are readily soluble in organic solvents; (V) and (VII) dissolve in hot water and (VIII) is very easily soluble in cold water.

(IV) is also obtained by the action of sodium methylate on the acyl chloride of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid, according to the system

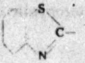
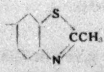
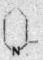


The diethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid was obtained in a similar manner but it was not possible to obtain esters of (V) and (VII) from the acyl chlorides of N-(2-thiazolyl)- and N-(2-pyridyl)-carbamido-N'-phosphoric acids.

The diphenyl ester of isocyanatophosphoric acid also readily reacts with amines of the heterocyclic series with the formation of N-heterocyclic derivatives of the diphenyl ester of carbamido-N'-phosphoric acid. The compounds obtained, their yield, melting points and analytical data are given in Table 3.

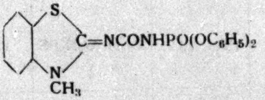
TABLE 3

Compounds of the Type $(C_6H_5O)_2PONHCONHR$

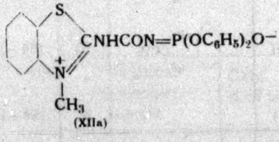
| No. of compound | R | Yield (as %) | Melting point | Found % N | Empirical formula | Calc. % N |
|---|---|---|---|---|---|---|
| (IX) |  | 99 | 165—166° | 9.63. 9.77 | $C_{20}H_{16}O_4N_3PS$ | 9.88 |
| (X) |  | 85 | 194—195 | 9.58. 9.60 | $C_{21}H_{18}O_4N_3PS$ | 9.56 |
| (XI) |  | 89 | 111—113 | 10.01. 10.95 | $C_{18}H_{16}O_4N_3P$ | 11.37 |

Compounds (IX-XI) are colorless crystalline compounds. They are soluble in alkalis but their characteristic properties are far less definite than in the case of the corresponding dimethyl esters: (XI) dissolves only in concentrated hydrochloric acid whereas (IX) and (X) do not react with hydrochloric acid.

When methylated by dimethylsulfate the diphenyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid (IX) forms a compound which splits off acid very easily when treated with alcohol or water. The substance obtained by this means may have the structure of (XII) or (XIIa):

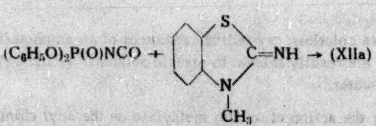


(XII)

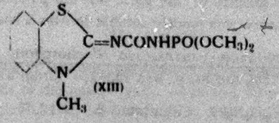


(XIIa)

The betaine structure (XIIa) is the more probable since the compound is difficultly soluble in alkali and does not react with acid. The same substance is obtained by the reaction of the diphenyl ester of isocyanatophosphoric acid with 3-methyl-2-benzothiazoloneimine.



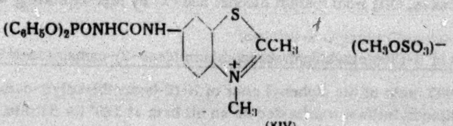
The methyl ester of isocyanatophosphoric acid also reacts readily with 3-methyl-2-benzothiazoloneimine. The reaction product is a colorless crystalline substance soluble in alkali and in acid. It most probably has the structure of (XIII).



(XIII)

It was not possible to obtain compound (XIII) by the methylation of the dimethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid (IV) since the reaction product was very easily decomposed by water with the formation of carbon dioxide and 3-methyl-2-benzothiazoloneimine.

When reacted with dimethylsulfate the diphenyl ester of N-(2-methylbenzothiazolyl-6)-carbamido-N'-phosphoric acid (X) forms a quaternary salt (XIV) which can form dyes when condensed with p-dimethylaminobenzaldehyde or orthoformic ester.



(XIV)

## EXPERIMENTAL

*Preparation of acyl chlorides of the type $Cl_2PONHCONHR$.* An ethereal solution of an equimolecular amount of amine was added dropwise with cooling to an ethereal solution of 0.01 mole of the acyl chloride of isocyanatophosphoric acid. The reaction product was precipitated in the form of a colorless finely-crystalline powder which was separated on a vacuum filter and washed with ether.

*The acyl chloride of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid* was obtained with a yield of 92%; the temperature of decomposition was 152-154°.

Found: equiv. (after hydrolysis) 3.89. $C_8H_6O_2N_3PSCl_2$. Calculated: equiv. 4.00 (as a result of hydrolysis the suspension of the acyl chloride in water became slightly heated).

*The acyl chloride of N-(2-thiazolyl)-carbamido-N'-phosphoric acid* was obtained with a yield of 92%. The substance deliquesced in air, giving off hydrogen chloride.

*The acyl chloride of N-(2-pyridyl)-carbamido-N'-phosphoric acid* was obtained in the form of a colorless, voluminous precipitate with a yield of 82%. The product rapidly decomposed in air. As a result of the hydrolysis of the acyl chloride by water at room temperature N-(2-pyridyl)-carbamido-N'-phosphoric acid (III) was formed. When 1.2 g of the acyl chloride was heated to boiling in 20 ml of water the initial product dissolved. After the cooled solution had been neutralized with alkali a colorless precipitate with an m. p. of 176-177° (from alcohol) was formed. In a mixed melt with 2-pyridylurea, obtained by the known method [3], the product showed no depression of the melting point.

*The preparation of acids of the type $RNHCONHPO(OH)_2$.* 0.01 mole of the acyl chloride of $Cl_2PONHCONHR$ was added in stages to 20 ml of water at room temperature. After 10-20 min the hydrolysis product was filtered on a vacuum filter, washed with alcohol and ether and purified by reprecipitating with hydrochloric acid from alkaline solution.

*The dimethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid (IV).* A solution of 0.02 mole of 2-aminobenzothiazole in ether was added gradually with cooling to an ethereal solution of 0.02 mole of the acyl chloride of isocyanatophosphoric acid. A solution of sodium methylate in methyl alcohol (from 0.06 mole of sodium and 25 ml of methyl alcohol) was added dropwise to the suspension of the acyl chloride of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid which was obtained. After an hour the reaction mixture was treated with water and the aqueous layer was separated and neutralized with hydrochloric acid. The reaction product came out in the form of an oil which rapidly solidified; the yield was 3.3 g (55.0%). The product was purified by crystallizing from benzene. The substance was readily soluble in alkali and in dilute hydrochloric acid.

The diethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid was obtained in a similar manner to the dimethyl ester. The yield was 18%, the m. p. was 153-154° (from alcohol).

Found %: N 12.65, 12.43. $C_{12}H_{16}O_4N_3PS$. Calculated %: N 12.76.

The reaction of the dimethyl ester of isocyanatophosphoric acid with amines of the heterocyclic series. An ethereal solution of the amine was added dropwise with cooling to a solution of the dimethyl ester of isocyanatophosphoric acid in ether. The reaction product was precipitated immediately as a crystalline deposit or an oil which rapidly crystallized. Compounds (IV) and (V) were crystallized from benzene, (VI) from methyl alcohol, (VII) from water and (VIII) from dichloroethane.

The reaction of the diphenyl ester of isocyanatophosphoric acid with amines of the heterocyclic series was carried out in the same way as for the dimethyl ester of isocyanatophosphoric acid. Substance (IX) was purified by crystallizing from benzene, (XI) from methyl alcohol and (X) by reprecipitating with ligroin from a solution in chloroform.

The diphenyl ester of N-(3-methyldihydrobenzothiazolidene-2)-carbamido-N'-phosphoric acid (XII).

a) A mixture of 0.002 mole of the diphenyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid (IX) and 0.003 mole of dimethylsulfate was heated on an oil bath at 120° for 30 min. The transparent viscous mass which was formed was washed with ether. When treated with alcohol the substance was converted into a colorless crystalline powder; the yield was 0.55 g (63.0%). After it had been recrystallized from alcohol the m. p. was 198-200°.

Found %: N 9.47, 9.42. $C_{21}H_{18}O_4N_3PS$. Calculated %: N 9.56.

b) When ethereal solutions of equimolecular amounts of the diphenyl ester of isocyanatophosphoric acid and 3-methyl-2-benzothiazoloneimine were mixed the reaction product separated out immediately in the form of a colorless crystalline precipitate. After recrystallizing from methyl alcohol the compound had a m. p. of 198-200° and showed no depression of the melting point in a mixed melt with the product obtained in the previous experiment.

The dimethyl ester of N-(3-methyldihydrobenzothiazolidene-2)-carbamido-N'-phosphoric acid (XIII). When ethereal solutions of 0.01 mole of 3-methyl-2-benzothiazoloneimine and 0.01 mole of the dimethyl ester of isocyanatophosphoric acid were mixed (XIII) was immediately precipitated; the yield was 2.8 g (83.0%). The substance was readily soluble in methyl and ethyl alcohols; it crystallized from water in the form of colorless platelets with a m. p. of 197-198° and was readily soluble in concentrated hydrochloric acid and in solutions of caustic alkalis.

Found %: N 13.50, 13.31. $C_{11}H_{14}O_4N_3PS$. Calculated %: N 13.33.

The reaction of the dimethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid (IV) with dimethylsulfate. A mixture of 0.002 mole of the dimethyl ester of N-(2-benzothiazolyl)-carbamido-N'-phosphoric acid and 0.003 mole of dimethylsulfate was heated on a water bath for 2 hrs, a glassy transparent mass being formed. When the reaction product was treated with water a vigorous emission of gas bubbles occurred. After the aqueous solution had been made alkaline a colorless precipitate of a substance with an m. p. of 120° (from alcohol) was formed. The compound showed no depression of the melting point in a mixed melt with 3-methyl-2-benzothiazoloneimine [4]; the yield was 0.15 g (14.0%).

3-Methylmethosulfate of the diphenylester of N-(2- methylbenzothiazole-6)-carbamido-N'-phosphoric acid (XIV). A mixture of 0.003 mole of the diphenyl ester of N-(2-methylbenzothiazolyl-6)-carbamido-N'-phosphoric acid (X) and 0.3 ml of dimethylsulfate was heated at 120° on an oil bath. The reaction mass first became liquid and then solidified. When the solid product had cooled it was washed with ether; the yield was 1.69 g (100.0%). It was in the form of colorless needles with a temperature of decomposition of 195-197° (from methyl alcohol). When heated the substance dissolved in water.

Found %: N 7.11, 7.26. $C_{23}H_{24}O_3N_3PS_2$. Calculated %: N 7.43.

## SUMMARY

The reaction of the acyl chloride of isocyanatophosphoric acid and also the methyl and diphenyl esters of isocyanatophosphoric acid with amines of the heterocyclic series was investigated. The chemical properties of the substances obtained were studied.

## LITERATURE CITED

[1] A. V. Kirsanov and E. S. Levchenko, J. Gen. Chem. 26, 2285 (1956).*

[2] A. V. Kirsanov and I. N. Zhmurova, J. Gen. Chem. 27, 1002 (1957).*

[3] M. P. Gerchuk and S. Z. Taits, J. Gen. Chem. 20, 910 (1950).*

[4] R. F. Hunter, J. Chem. Soc. 1926, 1391.

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* Original Russian pagination. See C.B. Translation.

# SYNTHESES BY MEANS OF ACRYLONITRILE

## XXXI. CYANOETHYLATION OF α-AMINO ACIDS AND GLYCYL GLYCINE BY β-CHLOROPROPIONITRILE

A. P. Terentyev and P. F. Butskus

The cyanoethylation of an entire series of compounds by means of β-chloropropionitrile has been described in literature. In the present paper we give the results of our experiments on the action of β-chloropropionitrile on α-amino acids and glycyl glycine. Until now only the cyanoethylation of the latter compounds with the use of acrylonitrile has been described [1-3].

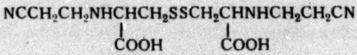
The cyanoethylation of α-amino acids and glycyl glycine by β-chloropropionitrile proceeds smoothly in the cold with evolution of heat, according to the system

$$HOOCCH(R)NH_2 + ClCH_2CH_2CN \rightarrow HOOCCH(R)NHCH_2CH_2CN + HCl$$

$$HOOCCH_2NHCOCH_2NH_2 + ClCH_2CH_2CN \rightarrow$$
$$\rightarrow HOOCCH_2NHCOCH_2NHCH_2CH_2CN + HCl$$

The reaction is carried out in aqueous solution with a slight excess of β-chloropropionitrile in the presence of an amount of base sufficient to combine with the acid groups of the cyanated compound and the hydrogen chloride during the process of the reaction. The yield of the cyanoethylation products is 70-96%.

When the amount of β-chloropropionitrile allowed to react on cystine is twice that of the latter, N,N'-di-(cyanoethyl)-cystine (I) is formed, which like other N-cyanoethylated α-amino acids does not give a ninhydrin reaction and does not contain amine nitrogen when determined by Van-Sleyk's method.



$$NCCH_2CH_2NH\underset{\displaystyle COOH}{\underset{|}{C}}HCH_2SSCH_2\underset{\displaystyle COOH}{\underset{|}{C}}HNHCH_2CH_2CN$$

(I)

Cyanoethylation by means of β-chloropropionitrile can proceed either by direct substitution of halogen, i. e., by a type of alkylation, or by an intermediate stage in which acrylonitrile is formed. The cyanoethylation of α-amino acids and glycyl glycine by β-chloropropionitrile evidently proceeds according to the second type of reaction because when β-chloropropionitrile was acted on by caustic potash, trimethylamine and triethylamine under similar conditions a 32-60% yield of acrylonitrile, and also potassium chloride, trimethylamine hydrochloride and triethylamine were obtained. When pyridine was used negative results were obtained.

## EXPERIMENTAL

1. N-Cyanoethyl-glycocoll. 6 g of triethylamine was added to a solution of 2 g of glycocoll in 10 ml of water and 3 g of β-chloropropionitrile was then added gradually with cooling and stirring. After it had been shaken for 2 hrs and left overnight the solution was evaporated to dryness under vacuum. 8-10 ml of water was added to the dry residue and the solution once more evaporated to dryness. The solid residue was dissolved in a small amount of water and the N-cyanoethyl-glycocoll was precipitated by the addition of 95% alcohol. The

yield was 3.1 g (86.1%). The m. p. was 192-193° (with decomp.). Data in literature [1] give the m. p. as 190-191° (decomp.). N-cyanoethyl-glycocoll did not give a reaction with ninhydrin and did not contain amine nitrogen when determined by Van Sleyk's method.

Found %: N 21.72, 21.53. $C_5H_8O_2N_2$. Calculated %: N 21.86.

**2. N-Cyanoethyl-alanine.** 10 g of triethylamine and 4.8 g of β-chloropropionitrile was added to a solution of 4 g of alanine in 20 ml of water. The reaction conditions and the method used for isolating the product were the same as in experiment 1. The yield of N-cyanoethyl-alanine was 5.5 g (87.3%). The m. p. was 249-250° (with decomp.) which corresponds to literature data [1].

Found %: N 19.60, 19.41. $C_6H_{10}O_2N_2$. Calculated %: N 19.71.

**3. N-Cyanoethyl-α-aminobutyric acid.** 14.5 g of triethylamine and 6.7 g of β-chloropropionitrile were added to a solution of 7 g of α-aminobutyric acid in 30 ml of water. The reaction conditions and the method used for isolating the product were the same as in experiment 1. The yield of N-cyanoethyl-α-aminobutyric acid was 9 g (84.9%). The m. p. was 233-235° (with decomp.).

Found %: N 17.74, 17.66. $C_7H_{12}O_2N_2$. Calculated %: N 17.90.

**4. N,N'-Di-(cyanoethyl)-cystine.** 25 ml of water and 3.9 g of caustic potash were added to 4 g of cystine and 3.3 g of β-chloropropionitrile was then added to the mixture with cooling and stirring. After it had been shaken for 2 hrs and kept overnight the reaction mixture was neutralized with 2.8 ml of 36% hydrochloric acid. The precipitate of N,N'-di-(cyanoethyl)-cystine which was formed was filtered and washed with water and with alcohol. The yield was 5.5 g (96.5%). The m. p. was 207-208° (with decomp.).

Found %: C 41.43, 41.31; H 5.33, 5.26; N 16.09, 16.10. $C_{12}H_{18}O_4N_4S_2$. Calculated %: C 41.60; H 5.24; N 16.17.

**5. N-Cyanoethyl-β-phenylalanine.** 10 ml of water, 1.5 g of caustic potash and 1.3 g of β-chloropropionitrile were added to 2 g of phenylalanine. The reaction conditions and the method used for isolating the product were the same as in experiment 4. The yield of N-cyanoethyl-phenylalanine was 2.4 g (92.3%). The m. p. was 228-230° (with decomp.), which corresponds to literature data [1].

Found %: N 12.63, 12.58. $C_{12}H_{14}O_2N_2$. Calculated %: N 12.83.

**6. N-Cyanoethyl-tyrosine.** 5 ml of water, 1 g of caustic potash and 0.6 g of β-chloropropionitrile were added to 1 g of tyrosine. The reaction conditions and the method used for isolating the product were the same as in experiment 4. The yield of N-cyanoethyl-tyrosine was 1.2 g (92.3%). The m. p. was 238-239° (with decomp.), which corresponds to literature data [1].

Found %: N 11.84, 11.86. $C_{12}H_{14}O_3N_2$. Calculated %: N 11.96.

In experiments 4-6 the reaction proceeded in a similar manner if trimethylamine and triphenylamine were used instead of caustic potash. The yields of the cyanoethylation products were the same.

**7. N-Cyanoethyl-glycyl glycine.** 8.1 g of triethylamine and 3.9 g of β-chloropropionitrile were added to a solution of 5 g of glycyl glycine in 30 ml of water. The reaction conditions and the method used for isolating the product were the same as for experiment 1. The yield of N-cyanoethyl-glycyl glycine was 4.9 g (70%). The m. p. was 143-144°.

Found %: N 22.40, 22.49. $C_7H_{11}O_3N_3$. Calculated %: N 22.69.

**8. The action of caustic potash and triethylamine on β-chloropropionitrile.** The experiments were carried out under conditions similar to those used for the cyanoethylation of α-amino acids and glycyl glycine by β-chloropropionitrile.

a) 15 g of β-chloropropionitrile was added to a solution of 9.4 g of caustic potash in 30 ml of water. The upper layer was washed with a small amount of sodium chloride solution and was then dried by calcium chloride and distilled. The yield of acrylonitrile was 5.5 g (61.8%). The b. p. was 77-78°. The lower aqueous layer was concentrated under vacuum and treated with a mixture of alcohol and ether. The precipitate of calcium chloride was filtered and washed with a mixture of alcohol and ether. The yield was 10.4 g (83.2%).

b) 15 g of β-chloropropionitrile was added to a solution of 16.9 g of triethylamine in 30 ml of water. The upper layer was lightly washed with acidified water, a small amount of sodium chloride solution, dried with calcium chloride and distilled. The yield of acrylonitrile was 5.4 g (60.7%). The b. p. was 77-78°. The lower aqueous layer was evaporated almost to dryness under vacuum and the residue was separated and washed with ether. The yield of triethylamine hydrochloride was 18.4 g (80.3%). The m. p. was 253-254°.

When an aqueous solution of trimethylamine and also solid caustic potash, anhydrous trimethylamine and triethylamine were allowed to act on β-chloropropionitrile, a 60-62% yield of acrylonitrile was obtained.

## SUMMARY

1. A method for the cyanoethylation of α-amino acids and glycyl glycine by β-chloropropionitrile was developed. N-cyanoethyl-β-aminobutyric acid and N,N'-di-(cyanoethyl)-cystine were obtained for the first time.

2. The suggestion was advanced that the cyanoethylation of α-amino acids and glycyl glycine proceeds through an intermediate stage in which acrylonitrile is formed.

## LITERATURE CITED

[1] L. L. McKinney, E. H. Uhing, E. A. Setzkorn, and J. C. Cowan, J. Am. Chem. Soc. 72, 2599 (1950).

[2] L. L. McKinney, E. H. Uhing, E. A. Setzkorn, and J. C. Cowan, J. Am. Chem. Soc. 73, 1641 (1951).

[3] A. P. Terentyev and P. F. Butskus, Proc. Acad. Sci. USSR 97, 851 (1954).

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# THE SYNTHESIS OF AROMATIC ANTIMONY COMPOUNDS

## VIII. THE PREPARATION OF p-TOLYL- AND β-NAPHTHALYLANTIMONY COMPOUNDS

A. B. Bruker

The method we have described for preparing phenyl- and p-fluorophenylantimony compounds by means of the corresponding arylhydrazines [1] was employed in the present work for the synthesis of p-tolyl- and β-naphthylantimony derivatives.

In the preparation of p-tolylantimony compounds we commenced with p-tolylhydrazine and antimony trichloride; the reaction between them was usually carried out in a medium of hydrochloric acid in the presence of cupric chloride and atmospheric oxygen. After appropriate treatment the precipitate formed by this reaction gave p-tolylstibine tetrachloride as well as p,p'-ditolyl and a small amount of di(p-tolyl)-stibine trichloride; the p-tolylstibine tetrachloride was isolated in the form of its double salt with ammonium chloride ($CH_3C_6H_4 \cdot SbCl_4NH_4Cl$). As a result of hydrolysis this substance was converted into p-tolyl antimonic acid; when the latter was reduced in a medium of hydrochloric acid p-tolylstibine dichloride was obtained.

p-Tolylstibine dichloride can be directly synthesized by the reduction with sulfur dioxide of the solution obtained after decomposing the precipitate formed during the reaction by means of hot hydrochloric acid.

β-Naphthylstibine tetrachloride, the double salt of β-naphthylstibine tetrachloride and ammonium chloride ($C_{10}H_7SbCl_4 \cdot NH_4Cl$), β-naphthylantimonic acid, β-naphthylstibine dichloride and β-naphthylstibine oxide were prepared in a similar manner.

The formation of secondary products was not observed in the case of the reaction with β-naphthylhydrazine.

It was earlier shown that when p-tolylstibine dichloride reacts with an equivalent amount of p-tolyl diazonium chloride a complex with the composition $CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2$, containing 1 mole of stibine chloride per mole of diazonium, is formed; when decomposed it gives ditolylstibine trichloride.

$$CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2 \rightarrow (CH_3C_6H_4)_2SbCl_3 + N_2$$

When this reaction is carried out with an excess of p-tolyl diazonium chloride a compound with the composition $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$, is formed, which when decomposed gives p-tolylstibine tetrachloride and ditolyl [2].

In the reaction of p-tolylhydrazine with $SbCl_3$, described in the present work, formation of secondary aromatic antimony compounds evidently takes place owing to the decomposition of the secondary complex $CH_3C_6H_4N_2Cl \cdot Cl_2SbC_6H_4CH_3$, and the process as a whole proceeds according to the equations given below, in agreement with the mechanism we have previously described [3].

$$CH_3C_6H_4NHNH_2 \cdot HCl + SbCl_3 + O_2 \xrightarrow[-2H_2O]{CuCl_2} \underset{\text{(Primary complex)}}{CH_3C_6H_4N_2Cl \cdot SbCl_3} \qquad (1)$$

$$CH_3C_6H_4NHNH_2 \cdot HCl + 2CH_3C_6H_4N_2Cl \cdot SbCl_3 \xrightarrow{CuCl_2}$$
$$\longrightarrow CH_3C_6H_4N_2Cl + 2CH_3C_6H_4SbCl_2 + 2N_2 + 4HCl \qquad (2)$$

$$CH_3C_6H_4N_2Cl + CH_3C_6H_4SbCl_2 \rightarrow \underset{\text{(Secondary complex)}}{CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2} \qquad (3)$$

$$CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2 \rightarrow (CH_3C_6H_4)_2SbCl_3 + N_2 \qquad (4)$$

The primary products are obtained by the decomposition of the complex $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$.

As regards the reaction of β-naphthylhydrazine and the intermediate compound formed during this reaction it is evident that in this instance the secondary complex $ArN_2Cl \cdot Cl_2SbAr$ is not formed and, therefore, only primary naphthylantimony compounds are formed by the decomposition of the complex with the composition $(\beta\text{-}C_{10}H_7N_2Cl)_2 \cdot \beta\text{-}C_{10}H_7SbCl_2$. The formation of the primary aromatic antimony compounds may be represented by the following series of equations.

$$ArNHNH_2 \cdot HCl + SbCl_3 + O_2 \xrightarrow{CuCl_2} ArN_2Cl \cdot SbCl_3 + 2H_2O \qquad (5) \qquad (5)$$

$$2ArN_2Cl \cdot SbCl_3 + ArNHNH_2 \cdot HCl \xrightarrow{CuCl_2} 2ArSbCl_2 + ArN_2Cl + 2N_2 + 4HCl \qquad (6) \qquad (6)$$

$$2ArN_2Cl + ArSbCl_2 \rightarrow (ArN_2Cl)_2 \cdot ArSbCl_2 \qquad (7) \qquad (7)$$

$$(ArN_2Cl)_2 \cdot ArSbCl_2 \rightarrow ArSbCl_4 + Ar_2 + 2N_2 \qquad (8) \qquad (8)$$

The following facts, observed during the present investigation, serve as a proof of this system.

1. The double compounds $(\beta\text{-}C_{10}H_7N_2Cl)_2 \cdot \beta\text{-}C_{10}H_7SbCl_2$ and $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$ were isolated by us directly by reacting β-naphthylhydrazine hydrochloride and p-tolylhydrazine with antimony trichloride.

2. The double compound $(\beta\text{-}C_{10}H_7N_2Cl)_2 \cdot \beta\text{-}C_{10}H_7SbCl_2$ was obtained by us from β-naphthylhydrazine and the double compound $\beta\text{-}C_{10}H_7N_2Cl \cdot SbCl_3$. We isolated the double compound $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$ by reacting p-tolylhydrazine hydrochloride and $CH_3C_6H_4Cl \cdot SbCl_3$.

3. We obtained the double compound $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$ by reacting p-tolylstibine dichloride with an excess of p-tolyldiazonium chloride [2].

4. The decomposition of these double compounds $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$ and $(\beta\text{-}C_{10}H_7N_2Cl)_2 \cdot \beta\text{-}C_{10}H_7SbCl_2$, obtained by the above-mentioned methods, gives primary derivatives of antimony and diaryls [Eq. (8)].

## EXPERIMENTAL

### The Reaction of p-Tolylhydrazine Hydrochloride, Antimony Trichloride and Cupric Chloride in a Hydrochloric-Acid Medium [*]

a) Preparation of the double compound $(CH_3C_6H_4N_2Cl)_2 \cdot CH_3C_6H_4SbCl_2$ (I). 28.5 g of antimony trichloride and 21.2 g of cupric chloride were dissolved with stirring in an open glass vessel. 20 g of p-tolylhydrazine hydrochloride was added to the solution obtained. After the precipitate had been stirred for 10-12 hrs it was washed on a filter with dilute hydrochloric acid, alcohol and ether.[**] The weight of the dry product was 15 g (40%, calculated on the antimony trichloride). It was a brown, odorless powder which melted at 115° (with decomp.) and gave a diazo reaction with β-naphthol; it was insoluble in the majority of organic solvents and decomposed in acetone with evolution of nitrogen.

Found %: Cl 26.0, 25.8; Sb 23.29, 23.6; N 7.9. $C_{21}H_{21}N_4Cl_4Sb$. Calculated %: Cl 23.9; Sb 20.3; N 9.4.[***]

b) Preparation of the double salt of p-tolylstibine tetrachloride and ammonium chloride $CH_3C_6H_4SbCl_4 \cdot NH_4Cl$ (II). When 5 g of the double compound (I) was boiled with 100 ml of dilute hydrochloric acid (1 : 2) nitrogen was liberated and the main reaction product was p-tolylstibine tetrachloride; a small amount of oil was also obtained together with p-ditolylstibine trichloride (m. p. 155°), which was formed by the presence of an admixture of $CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2$ in the investigated complex. Double the volume of a solution of ammonium chloride in concentrated hydrochloric acid (saturated in the cold) was added to the filtrate, obtained after the decomposition of the double compound. The precipitate formed was separated and dried in air. The product (about 3 g) was a yellowish powder which did not melt below 200°.

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[*] Carried out together with E. S. Makhlis.

[**] 2 g of p-tolylstibonic acid was obtained from the filtrate after the precipitate had been filtered.

[***] The difference between the values found and those calculated is explained by the presence of an admixture of the double compound $CH_3C_6H_4N_2Cl \cdot C_6H_4SbCl_2$.

Found %: Cl 41.4, 42.6; Sb 30.0, 30.4. $C_7H_{11}NCl_5Sb$. Calculated %: Cl 42.1; Sb 29.9.

**c) Preparation of p-tolylstibonic acid.** 2 g of the double salt (II) was treated with 500 ml of water. The p-tolylstibonic acid formed was separated, dried under vacuum and weighed. The yield was 1.2 g; the substance did not melt at less than 200°.

Found %: Sb 46.0, 46.7. $C_7H_9O_3Sb$. Calculated %: Sb 46.3.

**d) Preparation of p-tolylstibine dichloride from p-tolylstibonic acid.** 1 g of p-tolylstibonic acid was triturated with a few drops of alcohol. 2 ml of hydrochloric acid and 1 ml of water were then added. The solution obtained was filtered, 1-2 crystals of KI were added and it was then saturated with sulfur dioxide for half an hour at 0-2°. The precipitated white crystals were separated and dried. The yield was 0.9 g; the m. p. was 92-93°.

Found %: Cl 25.6, 25.6; Sb 43.0, 42.7. $C_7H_7Cl_2Sb$. Calculated %: Cl 25.0; Sb 42.8.

**e) Direct preparation of p-tolylstibine dichloride from the double compound (I).** 1-2 crystals of KI were added to the filtrate, obtained by the decomposition of 5 g of the double compound with dilute sulfuric acid (1 : 2), the solution was cooled to 0° and a current of sulfur dioxide was passed for 1 hr. The filtrate was filtered on a vacuum filter and the crystals obtained were dried. The yield was 1.3 g (56.5%); the m. p. was 92-93°.

**f) Formation of p,p'-ditolyl.** 1 g of the oil obtained by the decomposition of the double compound (I) (see section b) was dissolved in 50 ml of acetone. 150 ml of water was added to the solution obtained. The crystalline precipitate formed was separated, dried in air and recrystallized from alcohol. After recrystallization the substance melted at 121-122° which according to data in literature corresponds to p,p'-ditolyl.

## The Reaction of p-Tolylhydrazine Hydrochloride with the Double Compound of p-Tolyldiazonium Chloride and Antimony Trichloride.

**a) Preparation of the double compound (I).** 33 g of the double compound $CH_3C_6H_4N_2Cl \cdot SbCl_3$, 18 g of p-tolylhydrazine hydrochloride, 1 g of cupric chloride, 100 ml of hydrochloric acid and 200 ml of water were placed in a vessel equipped with a stirrer. After the mixture had been stirred for 60 hrs at room temperature the precipitate formed was separated and washed with dilute hydrochloric acid, alcohol and ether. After it had been dried over sulfuric acid in a desiccator the weight of the product was 15.5 g (60%). The product melted at 115° (decomp.) and gave a diazo reaction with $\beta$-naphthol. It was insoluble in the majority of organic solvents and decomposed in acetone with evolution of nitrogen.

Found %: Cl 25.3, 25.7; Sb 23.6, 23.8; N 8.5. $C_{21}H_{21}N_4Cl_4Sb$. Calculated %: Cl 23.9; Sb 20.3; N 9.4.

The difference in the analysis between the values found and those calculated is explained by the presence of a small amount of the double compound $CH_3C_6H_4N_2Cl \cdot CH_3C_6H_4SbCl_2$ in the product.

**b) Preparation of p,p'-ditolylstibine trichloride.** 5 g of the double compound was boiled with 100 ml of hydrochloric acid (1 : 2) and the solution was filtered from the oil which formed. White crystals of p,p'-ditolylstibine trichloride (0.3 g) with a m. p. of 155° were precipitated from the filtrate.

Found %: Cl 25.90, 25.09; Sb 29.6, 28.9. $C_{14}H_{14}Cl_3Sb$. Calculated %: Cl 25.3; Sb 29.7.

**c) Preparation of the double salt (II).** 2.8 g of the double salt (II), which does not melt at less than 200°, was obtained from 5 g of the double compound (I).

Found %: Cl 41.5, 42.6; Sb 30.0. $C_7H_{11}Cl_5NSb$. Calculated %: Cl 42.1; Sb 29.9.

d) Preparation of p-tolylstibonic acid. When 1 g of the double salt (II) was treated with 300 ml of water 0.7 g of p-tolylstibonic acid was obtained.

Found %: Sb 46.4, 46.3. $C_7H_9O_3Sb$. Calculated %: Sb 45.3.

e) Preparation of p-tolylstibine dichloride. 1.2 g of p-tolylstibine chloride was obtained from 2 g of p-tolylstibonic acid.

Found %: Cl 24.6, 25.5; Sb 42.14, 41.9. $C_7H_7Cl_2Sb$. Calculated %: Cl 25.0; Sb 42.8.

p-Tolylstibine dichloride was also obtained directly from the double compound (I). p,p'-Ditolyl with a m. p. of 121-122° was isolated from the oil obtained by the decomposition of the double compound.

### The Reaction of β-Naphthylhydrazine Hydrochloride, Antimony Trichloride and Cupric Chloride in a Hydrochloric-Acid Medium*

a) Preparation of the double compound $(\beta\text{-}C_{10}H_7N_2Cl)_2 \cdot \beta\text{-}C_{10}H_7SbCl_2$ (III). 100 ml of concentrated hydrochloric acid, 200 ml of water, 28.5 g of antimony trichloride and 22 g of cupric chloride were placed in a vessel. 24.8 g of β-naphthylhydrazine hydrochloride was added with stirring to the solution obtained. After the latter had been stirred for 18-20 hrs the precipitate formed was separated and washed with dilute hydrochloric acid, alcohol and ether. The dry product melted with decomposition at 98°; it gave a diazo reaction with β-naphthol and was insoluble in water, alcohol, ether, benzene, acetone and hydrochloric acid. The yield was 44-45 g (49-51%, calculated on the antimony trichloride).

Found %: Cl 21.47, 20.50; Sb 17.02, 17.93; N 7.00. $C_{30}H_{21}N_4Cl_4Sb$. Calculated %: Cl 20.26; Sb 17.40; N 7.90.

b) Preparation of the double salt $\beta\text{-}C_{10}H_7SbCl_4 \cdot NH_4Cl$ (IV) from the double compound (III). 5 g of the double compound (III) was boiled with 100 ml of dilute hydrochloric acid (1 : 2). The oil formed by the decomposition was separated from the liquid. A saturated solution of ammonium chloride in concentrated hydrochloric acid was added to the cooled filtrate. The yellow precipitate was filtered, washed with hydrochloric acid and dried. The double salt (IV) did not melt below 200°. The yield was 0.2-0.3 g (6-7%).

Found %: Cl 40.01, 39.56; Sb 26.98, 27.07. $C_{10}H_{11}NCl_5Sb$. Calculated %: Cl 39.02; Sb 27.41.

c) Preparation of β-naphthylantimonic acid (V). 1 g of the double salt (IV) was decomposed with 50 ml of water. The naphthylantimonic acid which was precipitated was separated and washed with water. It was a white powder which did not melt below 200°. The yield was 0.62 g (90%).

Found %: Sb 40.41, 40.14. $C_{10}H_9O_3Sb$. Calculated %: Sb 49.75.

d) Preparation of β-naphthylstibine dichloride (VI) from (V). 0.5 g of (V) was moistened with a small quantity of alcohol and treated with 12 ml of hydrochloric acid (2 : 1). The solution was filtered and 1-2 crystals of potassium iodide were added to the filtrate which was then saturated with sulfur dioxide. The precipitated chloride was separated and dried in air. The yield was 0.46 g (85%); the m. p. was 102°.

e) Preparation of (VI) from the double compound (III). 1-2 crystals of potassium iodide were added to the filtrate obtained by the decomposition of 5 g of the double compound (III) in 100 ml of dilute hydrochloric acid (1 : 2) and it was then reduced with sulfur dioxide gas at 0°. The precipitate of (VI) which was formed was recrystallized from petroleum ether and dried in air. The yield was 0.18 g (about 8%), the m. p. was 102°.

Found %: Cl 22.6, 22.0; Sb 37.49, 37.35. $C_{10}H_7Cl_2Sb$. Calculated %: Cl 22.18; Sb 38.08.

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* Carried out together with A. P. Shavikov.

f) Preparation of β-naphthylstibine oxide. 5 ml of alcohol and 20 ml of a 10% aqueous solution of ammonia were added to 0.5 g of (VI). The mixture obtained was heated for half an hour on a water bath. The pink crystals which were precipitated were separated and dried. The yield of β-naphthylstibine oxide was 0.35 g (88%). It melted with decomposition at 160°.

Found %: Sb 45.14, 45.44. $C_{10}H_7OSb$. Calculated %: Sb 45.98.

g) Formation of β,β'-dinaphthyl. 3 g of the oil obtained by the decomposition of the double compound (III) was boiled in 50 ml of alcohol on a water bath for 10-15 min. The alcoholic solution was filtered hot and diluted with water. The precipitate formed was separated, recrystallized from alcohol and dried in air; the β,β'-dinaphthyl melted at 187°. The yield was 0.3 g.

## The Reaction of β-Naphthylhydrazine Hydrochloride with the Double Compound of β-Naphthyldiazonium and Antimony Trichloride in the Presence of Cupric Chloride in a Hydrochloric-Acid Medium*

Preparation of the double compound (III). 300 ml of hydrochloric acid (1:2), 1 g of cupric chloride, 2 g of ferric chloride, 52.3 g of the double compound β-$C_{10}H_7N_2Cl \cdot SbCl_3$ and 24.8 g of β-naphthylhydrazine hydrochloride were placed in a vessel with a mechanical stirrer. After the mixture had been stirred for 35-40 hrs the precipitate obtained was separated, washed with dilute hydrochloric acid, alcohol and ether. The yield was 45-48 g (51-54%). From its analyses, properties and decomposition products the substance was the double compound (III).

When this double compound was decomposed β-naphthylstibine dichloride, β-naphthylstibine oxide, β-naphthylantimonic acid, the double salt of β-naphthylstibine tetrachloride and ammonium chloride and β,β'-dinaphthyl were formed.

## SUMMARY

It was shown that the method we had previously suggested for obtaining arylantimonic compounds may be used to obtain p-tolyl-β-naphthylantimonic compounds. When β-naphthyl- and p-tolylhydrazines react with antimony trichloride the main reaction products are primary aromatic antimony compounds. A mechanism for the reaction was proposed.

## LITERATURE CITED

[1] P. G. Sergeev and A. B. Bruker, J. Gen. Chem. 27, 2220 (1957);** A. B. Bruker, J. Gen. Chem. 27, 2223 (1957).**

[2] A. B. Bruker and E. S. Makhlis, J. Gen. Chem. 7, 1880 (1937).

[3] A. B. Bruker, Doklady Acad. Nauk SSSR 58, 803 (1947); J. Gen. Chem. 18, 1313 (1948).

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* Carried out together with A. P. Shavikov.

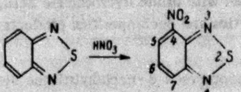
** Original Russian pagination. See C.B. Translation.

## STUDIES IN THE CHEMISTRY OF 2,1,3-THIODIAZOLE

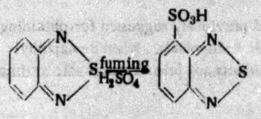
### V. NITRATION OF SOME MONO- AND DIHALO DERIVATIVES OF BENZO-2,1,3-THIODIAZOLE

V. G. Pesin and A. M. Khaletsky

**In a previous communication [1], we showed that benzo-2,1,3-thiodiazole is nitrated under conditions usual for aromatic compounds in which the nitro group attaches at position 4.**

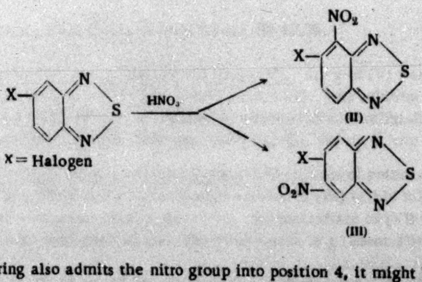


**L. S. Efros and R. M. Levit [2] showed that in sulfonation of benzo-2,1,3-thiodiazole the sulfo group also attaches at position 4.**



**Thus, in nitration and sulfonation, the thiodiazole ring admits the nitro- and sulfo-groups respectively, into position 4. It was of interest to study the effect of a halogen on the nitrating reaction. It is known that in nitration of chlorobenzene a mixture of the p- and o-nitrochlorobenzenes is formed with marked predominance of the p-isomer [3].**

**Since the p-position in 5-halobenzo-2,1,3-thiodiazole is occupied, the nitro group may enter positions 4 and 6.**

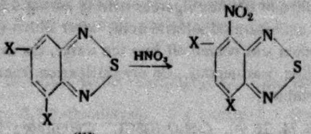


(II)

(III)

**Since the thiodiazole ring also admits the nitro group into position 4, it might be supposed that the nitration of 5-halobenzo-2,1,3-thiodiazole would favor formation of 4-nitro-5-halobenzo-2,1,3-thiodiazole (II); this was indeed confirmed by us.**

In the case of nitration of 5,7-dihalobenzo-2,1,3-thiodiazole, it appeared more probable that 4-nitro-5,7-dihalobenzo-2,1,3-thiodiazole would be formed, as was actually observed.

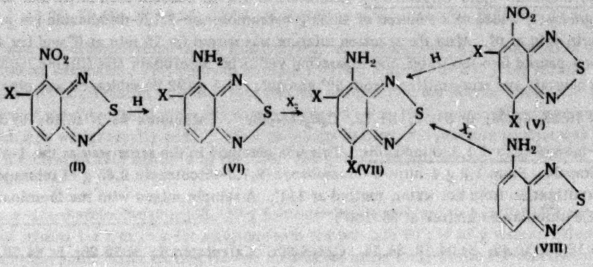


(IV) (V)

X = halogen

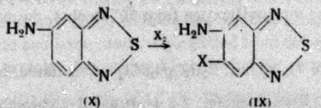
The position of the nitro group in the derivatives cited was verified by us through converse synthesis.

In the reduction of 5-halo-4-nitrobenzo-2,1,3-thiodiazoles(II) with iron filings in the presence of 2 % acetic acid, 5-halo-4-aminobenzo-2,1,3-thiodiazoles (VI) were obtained, which were converted by halogenation into 5,7-dihalo-4-aminobenzo-2,1,3-thiodiazoles (VII), identical in their properties both as reduction products of 5,7-dihalo-4-nitrobenzo-2,1,3-thiodiazoles (V) and as halogenation products of 4-aminobenzo-2,1,3-thiodiazole (VIII).



(II) (VI) (VII) (V) (VIII)

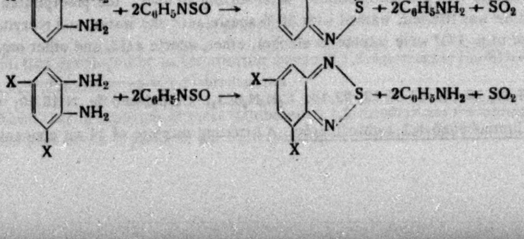
The position of the nitro group in (II) is also indicated by the fact that the reduction products of the latter, namely (VI), are not identical with 6-halo-5-aminobenzo-2,1,3-thiodiazoles (IX) obtained by halogenating 4-aminobenzo-2,1,3-thiodiazole (X).



(X) (IX)

Chlorination of 4-amino-5-chlorobenzo-2,1,3-thiodiazole (VI) was effected with dichloroamines in an acetic acid medium in the presence of concentrated hydrochloric acid; bromination of 4-amino-5-bromobenzo-2,1,3-thiodiazole (VI) was done with bromine in acetic acid medium.

The initial halogen- and dihalobenzo-2,1,3-thiodiazoles were obtained by reaction of 4-halogen- and 4,6-dihalogen-1,2-diaminobenzene with thionylaniline through our development of the earlier reactions of aromatic o-diamines with thionylaniline [4].



## EXPERIMENTAL

4-Nitro-5-chlorobenzo-2,1,3-thiodiazole. A nitrating mixture consisting of 1 ml concentrated nitric and 3 ml concentrated sulfuric acid was added at 0° with vigorous stirring during 0.5 hr to 2.5 g 6-chlorobenzo-2,1,3-thiodiazole (m.p. 57.5°) [5] in 10 ml concentrated sulfuric acid; after which the reaction mixture was stirred for 45 min. at 20°. After the reaction product was poured off into ice water, the separated precipitate was filtered and washed with cold water until reaction was neutral. On crystallization from 50° alcohol, 2.9 g of a yellowish substance of m.p. 141° (91.8%) was obtained.

Found %: N 19.67, 19.70; Cl 16.74, 16.60. $C_6H_2O_2N_3SCl$. Calculated %: N 19.5; Cl 16.47.

4-Amino-5-chlorobenzo-2,1,3-thiodiazole. 0.3 ml acetic acid and 1.15 g 4-nitro-5-chlorobenzo-2,1,3-thiodiazole (m.p. 141°) were successively introduced into a mixture of 4 g iron shavings and 25 ml water heated to boiling point with vigorous stirring. After 5 min boiling and subsequent cooling, the precipitate was filtered, washed with water, extracted with ether, and the solvent evaporated from the ether filtrate. We obtained 0.75 g of crystalline substance which after recrystallization from hot water melted at 92°. A sample mixed with the product obtained from the chlorination of 5-aminobenzo-2,1,3-thiodiazole melted at 92-102°.

Found %: N 22.64, 22.44; Cl 19.20, 19.37. $C_6H_4N_3SCl$. Calculated %: N 22.64; Cl 19.14.

4-Nitro-5-bromobenzo-2,1,3-thiodiazole. A mixture of 4.1 ml concentrated nitric and 13 ml concentrated sulfuric acid was gradually added to a solution of 10.35 g 5-bromobenzo-2,1,3-thiodiazole (m.p. 61°) [5] in 45 ml concentrated sulfuric acid at 0°. After the reaction mixture was stirred for 15 min at 0° and for 45 min at 20°, the reaction product was poured into ice water, the separating yellowish precipitate was filtered, washed with water until reaction was neutral, and recrystallized from 50° alcohol. 11.5 g (92 %) substance was obtained of m.p. 122°.

Found %: N 16.28, 16.06; Br 31.38, 31.12. $C_6H_2O_2N_3SBr$. Calculated %: N 16.15; Br 30.77.

4-Amino-5-bromobenzo-2,1,3-thiodiazole. This was obtained in the same way as the 4-amino-5-chlorobenzo-1,2,3-thiodiazole. From 1.2 g 4-nitro-5-bromobenzo-2,1,3-thiodiazole 0.85 g of substance was obtained which, after recrystallization from hot water, melted at 114°. A sample mixed with the bromination product of 5-aminobenzo-2,1,3-thiodiazole melted at 85-100°.

Found %: N 18.50, 18.42; Br 34.79, 34.54. $C_6H_2N_3SBr$. Calculated %: N 18.26; Br 34.78.

4-Nitro-5,7-dichlorobenzo-2,1,3-thiodiazole. A mixture of 3 ml concentrated nitric and 9 ml concentrated sulfuric acid was gradually added at 0° with constant stirring to a solution of 7.3 g of commercial 4,6-dichlorobenzo-2,1,3-thiodiazole (m.p. 93-97°) in 42 ml concentrated sulfuric acid. After stirring for 15 min at 0° and for 30 min at 20°, the reaction product was transferred to ice water, and the separating precipitate was filtered, washed with water to neutral, and dried. After recrystallization from 50° alcohol, the substance had m.p. 127-128°; yield quantitative.

Found %: N 16.75, 16.99; Cl 28.71, 28.59. $C_6H_3O_2N_3SCl_2$. Calculated %: N 16.80; Cl 28.40.

4-Amino-5,7-dichlorobenzo-2,1,3-thiodiazole. 1 g 4-nitro-5,7-dichlorobenzo-2,1,3-thiodiazole was introduced into a boiling mixture of 4 g iron filings, 25 ml water, and 0.5 ml acetic acid, and the reaction mixture was heated to the boiling point with vigorous stirring for 5 minutes. After cooling, filtering the precipitate, and washing it with water, the product was extracted with ether. When the ether was driven off from the filtrate, 0.78 g of substance was obtained; after this was purified by boiling with dilute hydrochloric acid (2 : 1) in the presence of carbon, and after it was alkalized with ammonia and washed with water, it melted at 171°. A sample mixed with the chlorination product of 4-aminobenzo-2,1,3-thiodiazole (m.p. 172.5-173°) melted at 171-172°.

Chlorination of 4-amino-5-chlorobenzo-2,1,3-thiodiazole. 1.5 ml of concentrated hydrochloric acid and 6 ml of acetic acid were gradually added at 12° (with stirring) to a mixture of this thiodiazole (m.p. 92°) with 6 ml of 98 % acetic acid and 0.65 g dichloroamine. After stirring an hour, the precipitated 4-amino-5,7-dichlorobenzo-2,1,3-thiodiazole was filtered, washed with 50 % acetic acid and water, and recrystallized from alcohol. The yellow needles of m.p. 171° were soluble in alcohol, ether, acetic acid, and other organic solvents, but not soluble in water.

Found %: N 19.06, 18.74; Cl 32.13, 32.18. $C_6H_3N_3SCl_2$. Calculated %: N 19.10; Cl 32.27.

4-Nitro-5,7-dibromobenzo-2,1,3-thiodiazole. A nitrating mixture of 17 ml concentrated sulfuric and 5.7

ml concentrated nitric acid was slowly added at 0° with stirring to a solution of 20 g 4,6-dibromobenzo-2,1,3-thiodiazole (m.p. 127-128°) in 70 ml of concentrated sulfuric acid. After 45 min stirring at 20-25° and standing overnight, the reaction product was placed in ice water; the separating precipitate was removed, washed with water until neutral, and dried. 22.3 g of substance was obtained with m.p. 155.5-156° (after recrystallization from 50° alcohol); yield 97 %.

Found %: N 12.38, 12.47; Br 47.28, 46.89. $C_6H_3O_2N_3SBr_2$. Calculated %: N 12.36; Br 47.20.

4-Amino-5,7-dibromobenzo-2,1,3-thiodiazole. 3 g 4-nitro-5,7-dibromobenzo-2,1,3-thiodiazole (m.p. 155.5-156°) was introduced into a boiling mixture of 1.5 ml acetic acid, 75 ml water, and 12 g iron filings, and the reaction mixture heated to the boiling point with vigorous stirring for 2-3 minutes; after this it was cooled in ice. After the precipitate was separated, washed with water, extracted with ether, and the latter removed, 2.5 g of a reddish-yellow substance was obtained (m.p. 160° after recrystallization from 50° alcohol).

Bromination of 4-amino-5-bromobenzo-2,1,3-thiodiazole. 0.77 g of this substance in 6 ml acetic acid was subjected to bromination with a solution of 0.2 ml bromine in 5 ml acetic acid for 15 minutes. After stirring an hour, the separating precipitate of 4-amino-5,7-dibromobenzo-2,1,3-thiodiazole was filtered, washed with 50 % acetic acid, and recrystallized from alcohol. Orange-colored crystals of m.p. 162-163° were obtained, which showed no depression in a test mixed with the substance obtained by brominating 4-aminobenzo-2,1,3-thiodiazole.

Found %: N 13.01; 13.09; Br 52.15, 51.66. $C_6H_3N_3SBr_2$. Calculated %: N 13.60; Br 51.78.

5-Bromo- and 4,6-dibromobenzo-2,1,3-thiodiazoles. a) Thionylaniline. A solution of 400 ml thionyl chloride in 400 ml toluene was added, with vigorous stirring, to 370 g aniline and 370 g dry toluene at the temperature of 50-60° (temperature of oil-bath), at such a rate that the temperature did not rise above that level. After addition of about one-third of the thionyl chloride, the bath was heated up to 100°, and at this temperature the remainder of the thionyl chloride was gradually added. After 25-30 hrs heating, the reaction product was pre-filtered through glass wool, and the clear filtrate distilled in vacuum. 468 g of thionylaniline was obtained, of m.p. 198-200°; yield about 85 %.

b) 4-Bromo-1,2-diaminobenzene [6]. 10 g 4-bromo-2-nitroaniline (m.p. 110-112°) was added in small lots with vigorous stirring for 1 hr to a hot solution (bath temperature 60°) of 39 g stannic chloride in 80 ml concentrated hydrochloric acid. After stirring for one hour at the same temperature the reaction mass was cooled and introduced into 300 ml of 30 % caustic soda. The separating 4-bromo-1,2-diaminobenzene was extracted with ether, and the ether evaporated. 7.5 g (88.1 %) of light-brown crystals was obtained.

c) 5-Bromobenzo-2,1,3-thiodiazole. 7.5 g commercial 4-bromo-1,2-diaminobenzene, 12 ml dry toluene, and 12 ml thionylaniline were heated with stirring over a boiling-water bath for 1 hr, after which the toluene was evaporated. The precipitate was treated with 4 % dilute hydrochloric acid, the separating product was filtered, washed with 5 % hydrochloric acid and water, and recrystallized from 60° alcohol. Yield 96.5 %, m.p. 61°. The colorless needles were insoluble in water, but soluble in alcohol, ether, benzene, and other organic solvents.

Found %: C 33.14, 33.93; H 1.69, 1.49; N 12.40, 12.44; S 14.43, 14.93; Br 37.56, 37.84. $C_6H_3N_2SBr$. Calculated %: C 33.50; H 1.39; N 13.02; S 14.89; Br 37.18.

d) 4,6-Dibromobenzo-2,1,3-thiodiazole. 50 g commercial 3,5-dibromophenylenediamine (m.p. 76-78°) obtained by the method of Jackson and Beggs [7], 50 ml dry toluene, and 54.4 g thionylaniline were heated for 1 hr over the boiling-water bath with vigorous stirring; on cooling, the separating crystals were filtered off and washed with alcohol. 44.82 g of crystals with m.p. 108-122° was obtained, and 1.2 g (98 %) crystals with m.p. 108-122° was obtained from the mother liquor. After recrystallization from alcohol, the m.p. was 127-128°. The colorless needles were insoluble in water, but soluble in organic solvents.

Found %: N 9.21, 9.43; S 10.67, 10.47. $C_6H_2N_2SBr_2$. Calculated %: N 9.52; S 10.88.

## SUMMARY

1. The earlier reaction developed by us for nitrating benzo-2,1,3-thiodiazole [1, 8] has been extended to 4-chloro-, 5-bromo-, 5,7-dibromobenzo-2,1,3-thiodiazoles.

2. It has been shown that in nitration of these halobenzo-2,1,3-thiodiazoles the nitro group displaces hydrogen in the $C_4$ position with 90-95 % yields of the corresponding nitro derivatives.

3. It has been shown that in the reduction of the nitrohaloderivatives of benzo-2,1,3-thiodiazole, the corresponding amines are formed in yields of 80-85%.

4. It has been shown that in chlorinating 4-amino-5-chlorobenzo-2,1,3-thiodiazole, 4-amino-5,7-dichlorobenzo-2,1,3-thiodiazole is formed, and in brominating 4-amino-5-bromobenzo-2,1,3-thiodiazole, 4-amino-5,7-dibromobenzo-2,1,3-thiodiazole is likewise formed.

## LITERATURE CITED

[1] A. M. Khaletsky and V. G. Pesin, J. Gen. Chem. 24, 133 (1954).*

[2] A. S. Efros and R. M. Levit, J. Gen. Chem. 25, 199 (1955).*

[3] N. N. Vorozhtsov, Principles of Synthesis of Intermediates and Dyes, (Goskhimizdat, Moscow, 1955).**

[4] A. M. Khaletsky et al., Proc. Acad. Sci. USSR, 106, 88 (1957).*

[5] V. G. Pesin et al., J. Gen. Chem. 27, 1575 (1957).*

[6] P. Ullmann, and F. Mauthner, Ber, 36, 4027 (1903).

[7] C. Jackson and S. Beggs, J. Am. Chem. Soc. 38, 685 (1916).

[8] A. M. Khaletsky and V. G. Pesin, J. Gen. Chem. 20, 1914 (1950).*

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